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## Studies Directed at the Synthesis of Trialkoxysilyl Substituted NLO Chromophores

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STUDIES DIRECTED AT THE SYNTHESIS OF TRIALKOXY-SILYL  
SUBSTITUTED NLO CHROMOPHORES

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science

By

IDA J. KUHR  
B.S., Wright State University, 1999

2000  
Wright State University

WRIGHT STATE UNIVERSITY  
SCHOOL OF GRADUATE STUDIES

August 1, 2000

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Ida J. Kuhr ENTITLED Studies Directed at the Synthesis of  
Trialkoxysilyl Substituted NLO Chromophores BE ACCEPTED IN PARTIAL  
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of  
Science.

Signed: William A. Feld, Ph.D.  
Thesis Director

Signed: Paul G. Seybold, Ph.D.  
Department Chair

Committee on Final Examination

Signed: Daniel D. Bombick, Ph.D.

Signed: M. Paul Serve', Ph.D.

Signed: William A. Feld, Ph.D.

Approved: Joseph F. Thomas, Jr., Ph.D.  
Dean, School of Graduate Studies

## ABSTRACT

Kuhr, Ida J. M.S., Department of Chemistry, Wright State University, 2000. Studies Directed at the Synthesis of Trialkoxysilyl Substituted NLO Chromophores.

The synthesis of trialkoxyalkyl substituted NLO chromophores has been investigated. The chromophore 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-2-fluorenyl)-benzothiazole was prepared by a five step process. Bromination of fluorene yielded 2,7-dibromo-fluorene which could be converted to 2,7-dibromo-9,9-diethylfluorene by alkylation with ethyl iodide in DMSO. Reaction of 2,7-dibromo-9,9-diethylfluorene with one equivalent of butyl lithium followed by reaction with DMF provides 2-bromo-7-formyl-9,9-diethylfluorene. Condensation of 2-bromo-7-formyl-9,9-diethylfluorene and 2-aminobenzenethiol in DMSO results in the formation of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole. The conversion of 3-hydroxydiphenylamine to 3-benzyloxy-diphenylamine was accomplished with benzyl bromide and potassium carbonate in DMF. A palladium catalyzed coupling of 3-benzyloxydiphenylamine and 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole provided 2-(7-(3-hydroxydiphenyl-amino)-9,9-diethyl-2-fluorenyl)benzothiazole. Several attempts to alkylate 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole with trimethoxysilylmethyl chloride were made but the alkylation product could not be isolated and appeared to be unstable.

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## **DEDICATION**

To my mom, Laura Barnett, who was always there to give me the support and guidance I needed in life. Thank you for all of the sacrifices you've made for me. Your generosity and love will never be forgotten. To my grandparents, Meyer and Betty Barnett, who encouraged me to pursue my goals. To Sam, who was always there to listen and smile. I love you all very much.

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## INTRODUCTION

An organic nonlinear optical material is a medium in which an internal charge separation on each molecule will form when an external electromagnetic field is applied. The induced dipole results in the polarization of these molecules, which form their own electric field. An intense external field produced by lasers will cause a disruption in the internally induced field of the molecules within the material. An intriguing nonlinear effect of this interaction is two-photon absorption. Molecules within the material undergo an electronic transition from a ground state to an excited state as they absorb two photons simultaneously. This transition is of interest because it occurs at a higher frequency than that of the original light absorbed. The phenomenon is known as the two-photon frequency-upconverted emission. One application for this phenomenon is sensor protection. Irradiation from an intense infrared laser source results in the nonlinear material within the sensor protective layer absorbing the beam and converting the intense infrared laser radiation into harmless visible light with less intensity, shielding the sensor.

The objective of this research was to synthesize 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl)fluorenylbenzothiazole and 2-(7-(3-methyltriethoxysiloxy)diphenylamino-9,9-diethyl)fluorenylbenzothiazole which are compounds believed to display two-photon absorption and subsequent frequency-upconverted emission.

## HISTORICAL

### Optical Nonlinearity in Organic Systems

Organic systems interacting with light are similar to a dielectric in an electric field and are treated by a theory known as the dipole approximation.<sup>1</sup> In other words, an applied external electromagnetic field interacting with an organic nonlinear optical material results in an internal charge separation on each molecule of that material. The dipole moment can be defined as:

$$\mu_{\text{ind}} = -e\mathbf{r}$$

$e$  - the electronic charge

$\mathbf{r}$  - the field induced displacement

The induced dipole causes a bulk polarization of the molecules in the material which creates an electric material.<sup>2</sup> A linear polarization of the bulk material is a result of a weak externally applied field<sup>3</sup> and is given by:

$$\mathbf{P} = \chi^{(1)}\mathbf{E}$$

$\chi^{(1)}$  – the first order nonlinear susceptibility for the bulk material

$\mathbf{E}$  – the applied electric field

$\mathbf{P}$  – the polarization of the bulk material

However, when an intense external field is applied, such as that produced by a laser, the electric field created can disrupt the internal field created by atoms within the material. The laser radiation and material are interrelated and can alter each other.<sup>2</sup> The

bulk polarization is no longer linear with respect to the applied field. It can be described in terms of a power series expansion of the applied field<sup>4</sup>,  $\mathbf{E}$ :

$$\mathbf{P} = \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}\mathbf{E} + \chi^{(3)} \mathbf{E}\mathbf{E}\mathbf{E} + \dots$$

$\chi^{(2)}$  – the second-order nonlinear susceptibility of the bulk material

$\chi^{(3)}$  – the third-order nonlinear susceptibility of the bulk material

These nonlinear susceptibilities are tensor quantities, which relate the polarization response in one direction to field components in three directions. Polarization in directions other than that of the applied electric fields can be produced because organic crystals are composed of molecules having definite orientations.<sup>3</sup> These nonlinear optical susceptibilities ( $\chi^{(n)}$ ) of an organic material are a result of the intricate electronic and molecular structures of the molecules.<sup>4</sup>

Nonlinear optical properties of the molecules within a material determine the optical nonlinearity of the bulk material. Microscopic polarizations of the molecules which make up the material determine the macroscopic polarization of the bulk material. When an externally induced radiation field<sup>3</sup> is applied to the material, the microscopic polarization response of the molecules is given by:

$$\mathbf{P}_I = \alpha_{ij} \mathbf{E}_j + \beta_{ijk} \mathbf{E}_j \mathbf{E}_k + \gamma_{ijkl} \mathbf{E}_j \mathbf{E}_k \mathbf{E}_l + \dots$$

$\mathbf{i}, \mathbf{j}, \mathbf{k}, \mathbf{l}$  – refer to the molecular coordinate system

$\mathbf{P}$  – the microscopic polarization of the applied field of the molecule

$\mathbf{E}_j, \mathbf{E}_k, \mathbf{E}_l$  – the components of the applied field

$\alpha$  - the polarizability term

$\beta$  - the first molecular hyperpolarizability term

$\gamma$  - the second molecular hyperpolarizability term

The polarizability term,  $\alpha$ , describes linear absorption and refraction which are a direct result of the interaction of the molecule with the optical field. The first and second terms,  $\beta$  and  $\gamma$  represent the second- and third-order nonlinear optical interactions, respectively. Both of these terms are sensitive to the electronic structure of the material.

Using the microscopic polarization of the molecules, the macroscopic polarization of the bulk material<sup>3</sup> is given by:

$$\mathbf{P}_I = \chi^{(1)}_{IJ} \mathbf{E}_J + \chi^{(2)}_{IJK} \mathbf{E}_J \mathbf{E}_K + \chi^{(3)}_{IJKL} \mathbf{E}_J \mathbf{E}_K \mathbf{E}_L + \dots$$

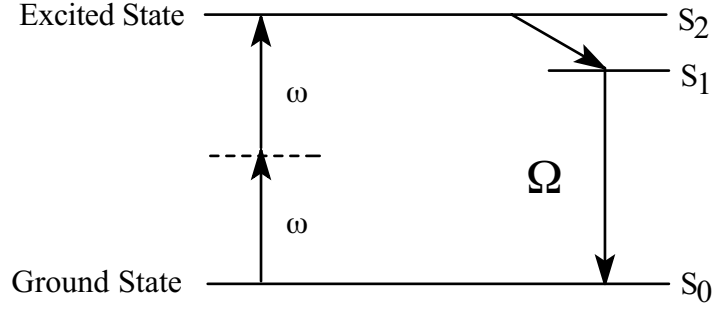
$I, J, K, L$  – refer to the coordinate system of the bulk material

$\mathbf{P}$  – the macroscopic polarization of the bulk material

$\mathbf{E}_J, \mathbf{E}_K, \mathbf{E}_L$  – the components of the applied field

$\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$  – the nonlinear susceptibilities the bulk material

The focus of this research is the third-order nonlinear susceptibility of the bulk material,  $\chi^{(3)}$ . The coefficients reveal how these materials can be used for various device applications. Nonresonant and resonant effects contribute to the term,  $\chi^{(3)}$ . The real part of nonlinearity or nonlinear refraction, is a result of nonresonant contributions to  $\chi^{(3)}$ . The imaginary part of nonlinearity, or nonlinear absorption, is a result of resonant contributions. One-photon absorption results in changes of index of refraction, which is mostly due to sample heating. Two-photon absorption is a process where the two atoms or molecules make a transition from the ground state to an excited state via simultaneous absorption of two laser photons (**Figure 1**).



**Figure 1.** Two-Photon Absorption and Emission

### Effects of the Nonresonant Contributions to $\chi^{(3)}$

The real part of nonlinearity or nonlinear refraction is the nonresonant effect of  $\chi^{(3)}$ . Self-action is an example of nonlinearity in which the intensity dependence of the refractive index causes the material to display nonlinear polarization at the same frequency as the incident beam. It is named “self-action”<sup>5</sup> because the nonlinear polarization created by the incident beam effects the properties of the same beam via an intensity-dependent refractive index.<sup>3</sup> As a result, the beam could self-focus, self-defocus, or its frequency broaden. The nonlinear polarization resulting from the self-action interaction<sup>5</sup> is given by:

$$\mathbf{P}_i(\omega) = 3/4 \text{Re}[\chi^{(3)}_{iikl}(-\omega; \omega, -\omega, \omega)] \mathbf{E}_i(\omega) |\mathbf{E}_k(\omega)|^2$$

$\mathbf{i}, \mathbf{j}, \mathbf{k}, \mathbf{l}$  – refer to the molecular coordinate system

$\mathbf{P}$  – the polarization of the molecule

$\mathbf{E}_i, \mathbf{E}_k$  – the components of the applied electric field

$\omega$  - the frequency of the incident beam

$\text{Re}$  – represents the real parts (refractivity) of  $\chi^{(3)}$



There is no exchange of energy between the optical field and the nonlinear medium since self-action is a nonresonant effect.

### **Effects of the Resonant Contributions to $\chi^{(3)}$**

The imaginary part of the nonlinearity, or nonlinear absorption is the resonant effect of  $\chi^{(3)}$ . Two photon absorption is the simultaneous absorption of two laser photons from the ground state ( ).<sup>6</sup> This is considered a third-order response possessing both electronic and vibrational resonance interactions from the real excited singlet state ( $S_2$ ). A nonradiative decay to a lower singlet state ( $S_1$ ) occurs followed by a one-photon radiative decay (fluorescence emission) to the ground state ( $S_0$ ). The key here is that the fluorescence occurs at a higher frequency  $\Omega$  (upconverted) than either of its two absorbed photons initial frequency  $\omega$ .<sup>3</sup> The two-photon absorption resemble self-action in that both can be stated in terms of nonlinear polarization<sup>5</sup>:

$$\mathbf{P}_I(\omega) = - \text{Im}[\chi^{(3)}_{iik}(-\omega; \omega, \omega, -\omega) \mathbf{E}_I(\omega) | \mathbf{E}_k(\omega) |^2]^*$$

$\mathbf{i}, \mathbf{k}$  – refer to the coordinate system of the bulk material

$\mathbf{P}$  – the polarization of the bulk material

$\mathbf{E}_i, \mathbf{E}_k$  – the components of the applied electric field

$\omega$  - the frequency of the incident beam

$\text{Im}$  – represents the imaginary part (absorption) of  $\chi^{(3)}$

Unlike self-action which involves the real part of the third-order nonlinear susceptibility, the two-photon absorption involves the imaginary part of the third order nonlinear susceptibility. This describes a decrease in the intensity of the incident beam in the medium resulting from an exchange of energy between the optical field and medium.

The intensity of the incident beam propagating in the z direction through the nonlinear medium<sup>7</sup> can be given by:

$$\delta I / \delta z = - (\alpha I + \beta I^2)$$

$\alpha$  - the linear absorption coefficient

$\beta$  - the two-photon absorption coefficient

If the incident intensity is low, the linear absorption coefficient  $\alpha$  is about zero.

The equation above can be rewritten in terms of transmitted intensity  $I(L)$  as a function of incident intensity,  $I_0$ <sup>7</sup>:

$$I(L) = I_0 / (1 + I_0 \beta L)$$

$L$  – the length of the sample

As the two-photon absorption coefficient,  $\beta$ , increases, the intensity of the transmitted light,  $I$ , decreases. The two-photon absorption coefficient for a material<sup>7</sup> is given by:

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d_0 \times 10^{-3}$$

$\sigma_2$  – the molecular cross-section of the two-photon absorption ( $\text{cm}^4/\text{GW}$ )

$N_0$  – the molecular sensity of the two-photon absorption compound

$N_A$  – Avogadro's number

$d_0$  – the concentration (m/L) of the two-photon absorption compound in the matrix

The product of the molecular cross-section of the two-photon absorption  $\sigma_2$  and the energy of the incident photon ( $h\omega$ ) results in a new equation<sup>7</sup>, where  $\sigma'_2$  can be expressed as:

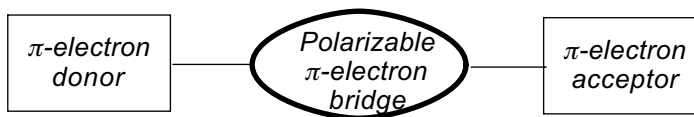
$$\sigma'_2 = h\omega\sigma_2$$

The new expression  $\sigma'_2$  exhibits an accurate and reproducible coefficient for the material's two-photon activity and is expressed in units of ( $\text{cm}^4 \cdot \text{sec} \cdot \text{ph}^{-1} \cdot \text{molecule}^{-1}$ ).

### **Molecules Designed for Third-Order Optical Nonlinearity**

The molecular structural requirements needed for improving the second molecular hyperpolarizability term  $\gamma$  and therefore the third-order nonlinear susceptibility of the bulk material  $\chi^{(3)}$  are not well known. One focus in the study of structure-property relationships is the use of theoretical models to predict factors leading to increased third-order behavior. Definite orientation of the molecules in bulk nonlinear material is not significant in third-order processes because the macroscopic third-order nonlinear response is an average of all possible orientations of the polarizable substituents and cancellation effects do not occur. However, orientation can improve the interaction of the polarizable unit with the field components if the polarizable unit displays a nonlinear response that is huge in one particular direction. This ultimately leads to an increase in the nonlinear response. In other words, a medium with all of its conjugated molecules or polymers aligned in the same direction can have a larger  $\chi^{(3)}$  value than an amorphous form of the same polymer.<sup>3</sup> In order to increase the hyperpolarizability density and  $\chi^{(3)}$ , molecules and polymer chains should be densely packed. These effects are further improved if the molecule possesses both an electronic acceptor and electronic donor. The overall lack of symmetry requirements expands the number of possible third-order organic structures to all materials including liquids, liquid crystals, and solids.<sup>3</sup> The electronic makeup of the nonlinear medium is very important since delocalized  $\pi$ -electron systems are very often associated with third-order nonlinearity.<sup>3</sup>

The current emphasis in molecular design for third-order structures is to work with systems that possess a  $\pi$ -electron bridge, and a heterocyclic  $\pi$ -electron acceptor (Figure 2).

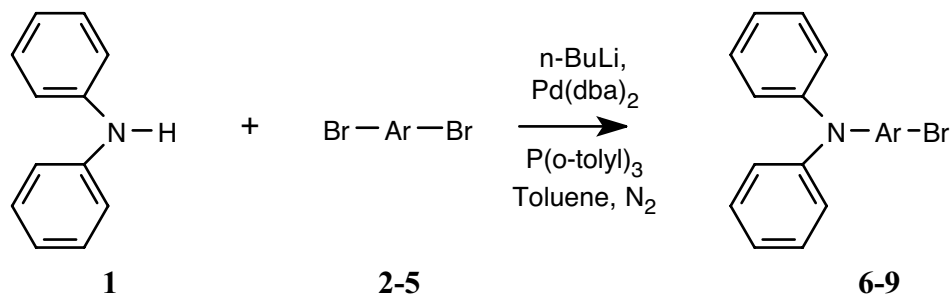


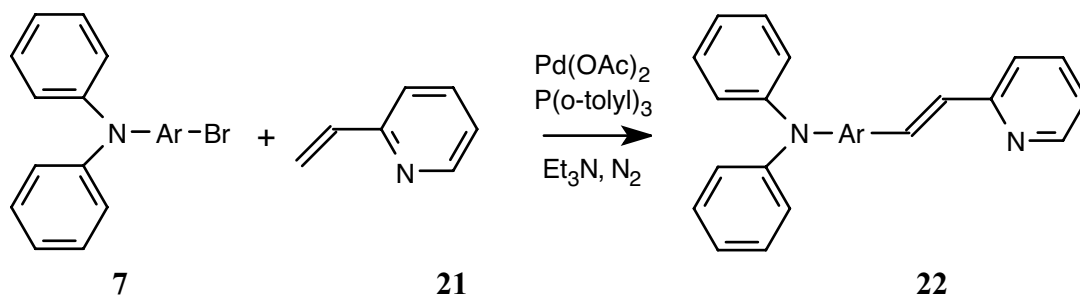
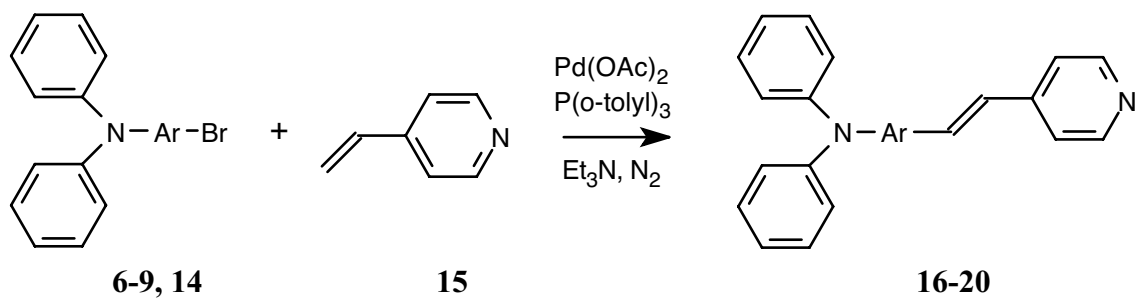
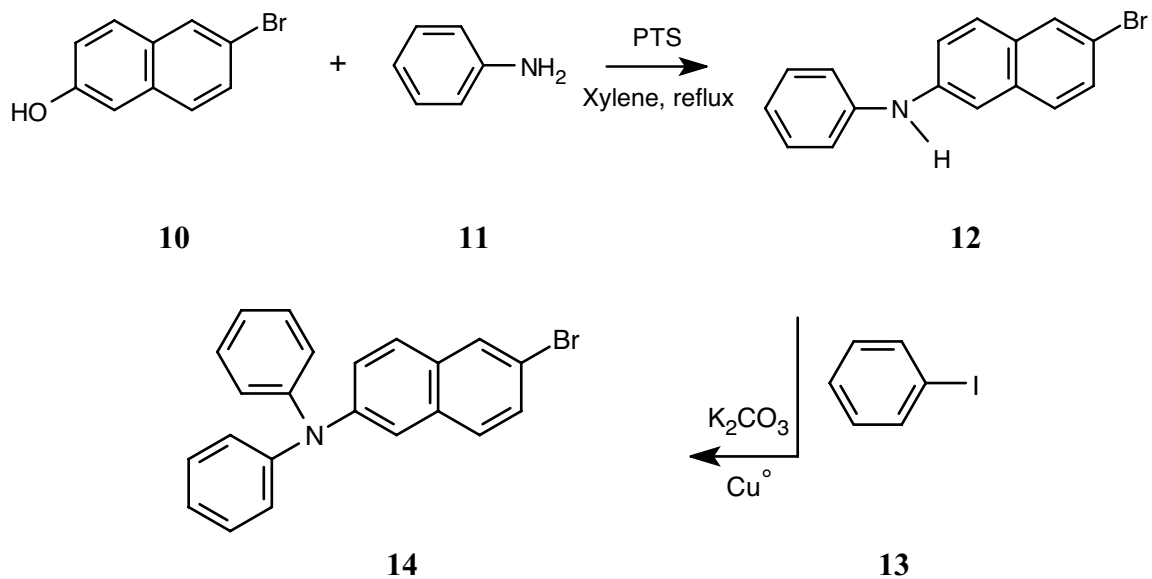
**Figure 2.** Molecular Components of Compounds Exhibiting Third-Order Nonlinearity

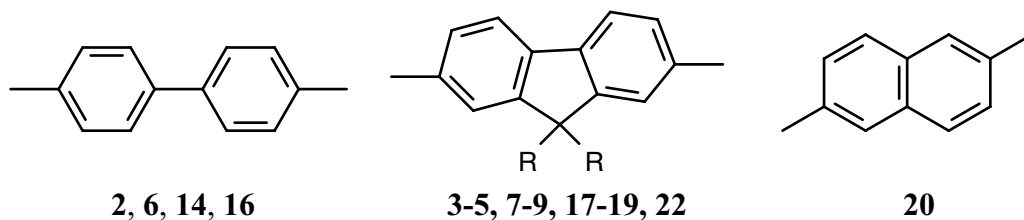
Other important structural factors include molecular linearity, planarity, effective conjugation length and the number of  $\pi$ -electrons considered. Molecular design focuses on using the effective molecular two-photon absorption cross-section. The cross-section is related to the imaginary part of the third-order nonlinear susceptibility of the medium at the two-photon absorption frequency.<sup>8</sup> The major challenge in design is to increase the two-photon absorption cross section without shifting the two-photon peak away from 800 nm.<sup>8</sup>

### Assymetric Materials Exhibiting Resonant Third-Order NLO Activity

A series of compounds with systematically varied molecular structures which exhibit very large and effective two-photon cross sections have been synthesized and







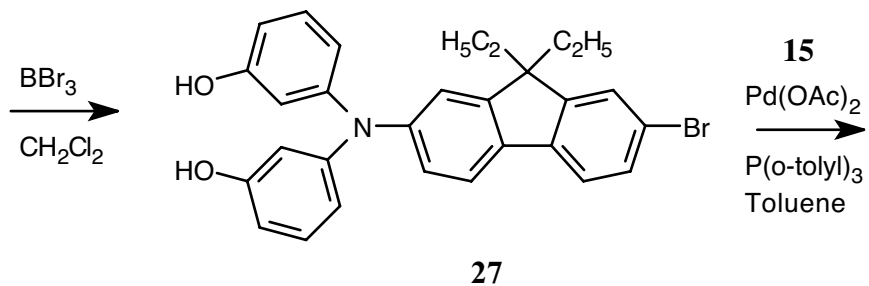
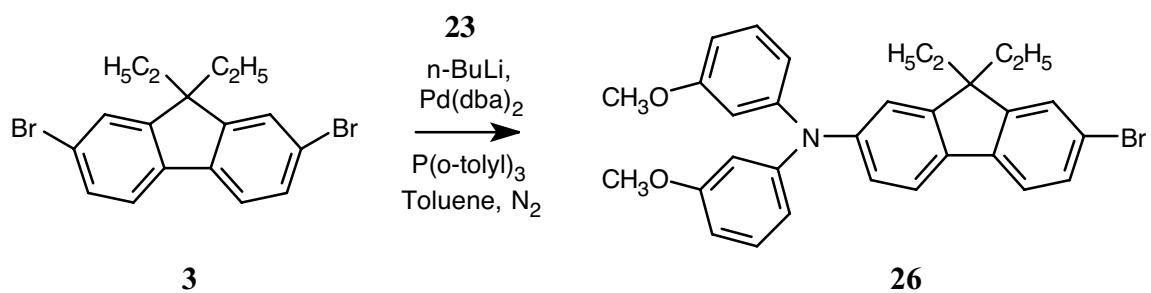
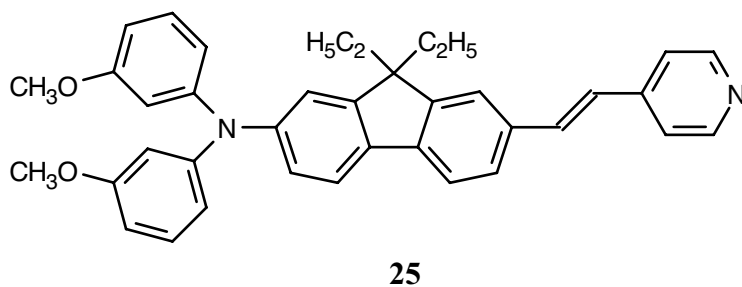
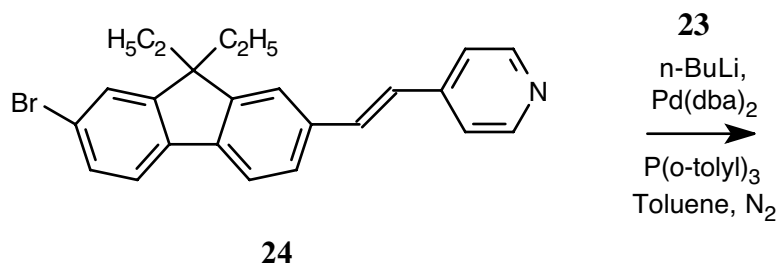
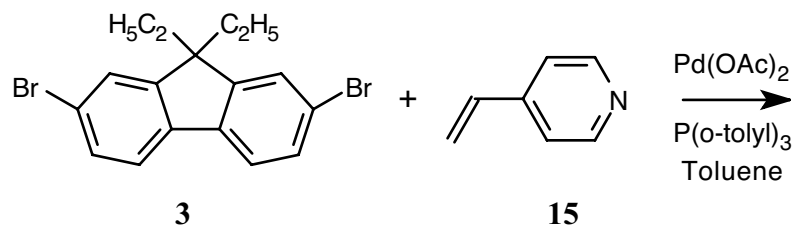
Compound	R
3, 7, 17, 22	C <sub>2</sub> H <sub>5</sub>
4, 8, 18	C <sub>6</sub> H <sub>13</sub>
5, 9, 19	C <sub>10</sub> H <sub>21</sub>

characterized using a nonlinear technique.<sup>8</sup> In the first set of chromophores<sup>8</sup>, diphenylamine **1** reacts with 4,4-dibromobiphenyl **2** or 2,7-dibromo-9,9-dialkyl-9H-fluorene **3-5** to yield 4-bromo-4'-(diphenylamino)biphenyl **6** and N,N-diphenyl-7-bromo-dialkyl-9H-fluorene-2-amine **7-9**. The condensation of 6-bromo-2-naphthol **10** and aniline **11** yields 6-bromo-N-phenyl-2-aminonaphthalene **12**. Compound **12** can be arylated with iodobenzene **13** to yield 6-bromo-N,N-diphenyl-2-aminonaphthalene **14**. Compounds **6-9** and **14** undergo a palladium catalyzed Heck reaction with 4-vinylpyridine **15** to give N,N-diphenyl-N-[4-[4-[2-(4-pyridyl)-1-ethenyl]phenyl]phenyl]amine **16**, N,N-diphenyl-7-(2-(4-pyridinyl)ethenyl)-9,9-diethyl-9H-fluorene-2-amine **17**, N,N-diphenyl-7-(2-(4-pyridinyl)ethenyl)-9,9-di-n-hexyl-9H-fluorene-2-amine **18**, N,N-diphenyl-7-(2-(4-pyridinyl)ethenyl)-9,9-di-n-decyl-9H-fluorene-2-amine **19**, and 2-(4-(6-(N,N-diphenylamino)-2-naphthyl)vinyl)pyridine **20**, respectively. Compound **7** also undergoes the the same palladium catalyzed Heck reaction with 2-vinylpyridine **21** to yield N,N-diphenyl-7-(2-(4-pyridinyl)ethenyl)-9,9-diethyl-9H-fluorene-2-amine **22**.

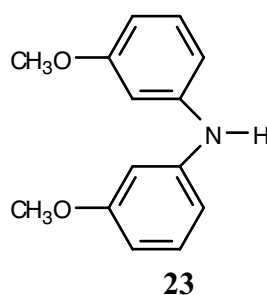
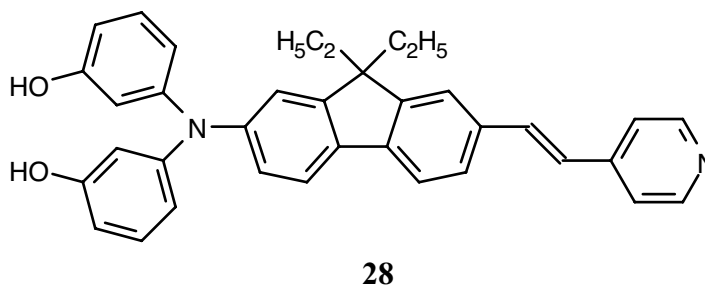
**Table 1.** Optical Properties of the Chromophores at 800 nm in THF

Compd .	$\lambda_{\text{max}}$ (nm) Linear Abs. (Upconv. Em.)	$\beta$ cm/GW @ 0.2 mol/L	$\sigma_2'$ ( $\times 10^{-48}$ cm <sup>4</sup> ·sec ph·molecule	$\sigma_2'$ ( $\times 10^{-50}$ cm <sup>4</sup> ·sec·mole ph·molecule·g
<b>16</b>	485	1.9	39.0	9.2
<b>17</b>	488	4.7	97.0	19.7
<b>18</b>	494	5.1	106.1	17.5
<b>19</b>	492	5.6	115.6	16.1
<b>20</b>	488	3.3	68.4	17.2
<b>22</b>	478	4.7	79.4	16.1
<b>25</b>	488	5.6	114.8	20.8
<b>28</b>	500	5.0	103	19.6
<b>30</b>	492	3.8	79.4	11.1
<b>33</b>	479	N/A	97.5	19

Compounds **16-20** and **22** all have a diphenylamine as the  $\pi$ -electron donor, a pyridine as the heterocyclic  $\pi$ -electron bridge and the  $\pi$ -electron acceptor which is used to increase the effective conjugation length of the system. They differ in the polarizable aromatic bridge that each compound possesses (**Figure 2**). As seen in **Table 1**<sup>8</sup>, compound **15** (biphenyl backbone) has the smallest observed two-photon cross section,  $\sigma_2'$ . Compounds **16-20** have a fluorene bridge and have a larger two-photon cross section than either **15** or **20**. The explanation for such behavior is not completely known. Compounds **17-19** differ in the pendant side chains that were initially used in the molecular design to increase solubility. As the pendant alkyl chain length increases from ethyl in **17** to n-hexyl in **18** to n-decyl in **19**, the two-photon absorption cross section increases as seen in **Table 1**. A possible reason for such behavior is that the steric hindrance of the longer alkyl chains inhibits aggregate formation. A change in the pyridine attachment position from the ortho- **22** to the para-position **17** extends conjugation length and results in an enhancement of the two-photon cross section<sup>8</sup> as seen in **Table 1**.







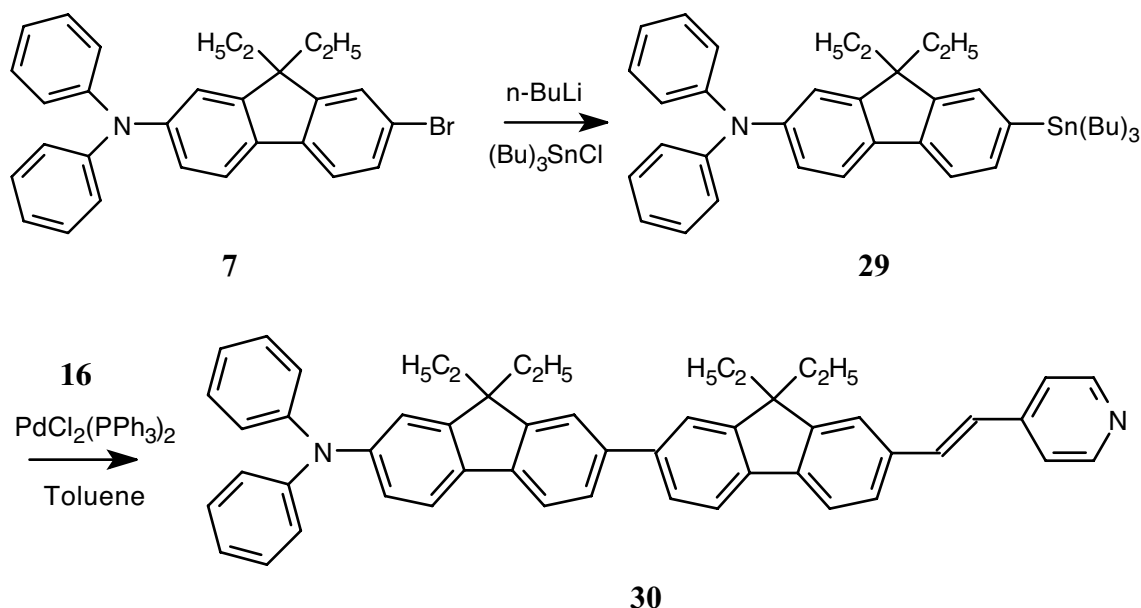
Changing the  $\pi$ -electron donor unit can alter the magnitude of the effective two-photon absorption cross section.<sup>8</sup> The synthesis of a second series of chromophores involves those containing substituted diphenylamino electron-donating groups coupled with fluorene bridges. A reaction scheme involving two different routes is involved.<sup>8</sup> The first route involves **3** undergoing a palladium catalyzed Heck reaction with 4-vinylpyridine to yield N,N-diphenyl-7-(2-(4-pyridinyl)ethenyl)-9,9-diethyl-9H-fluorene-2-amine **23**. Compound **23** reacts in a palladium catalyzed reaction with 3,3'-dimethoxydiphenylamine **24** to yield N,N-bis(3-methoxyphenyl)-N-{9,9-diethyl-7-[2-(4-pyridyl)-1-ethenyl]-9H-2-fluorenyl}amine **25**. Attempting to deprotect **25** to form the dihydroxy compound proved to be complicated, forming several byproducts. The alternative route involved reacting **3** with **24** to form N,N-bis(3-methoxyphenyl)-N-(7-bromo-9,9-diethyl-9H-2-fluorenyl)amine **26**. The synthesis of N,N-bis(3-

hydroxyphenyl)-7-bromofluorene-2-amine **27** involved the deprotection of **26** using boron tribromide. Compound **27** underwent a palladium catalyzed Heck reaction with **15** to form 3-(9,9-diethyl-7-[2-(4-pyridyl)1-ethenyl]-9H-2-fluorenyl)-3-hydroxyanilino)phenol **28**.

Increasing the electron density on the diphenylamino donor group increases the magnitude of the effective two-photon absorption cross-section in fluorene bridged chromophores. The behavior observed was somewhat surprising because the electron donating functional groups were not in a position on the phenyl rings that would allow direct conjugation with the amine nitrogen. The two-photon absorption cross section increased in going from the unsubstituted diphenyl amino compound **17** through the dihydroxy compound **28** to the dimethoxy compound **25**. The reasoning for this behavior is not fully understood. A possible reason might be that there is an increased aggregation in solution in this case brought about by the hydrogen bonding ability of the hydroxy groups with the pyridyl units.<sup>8</sup>

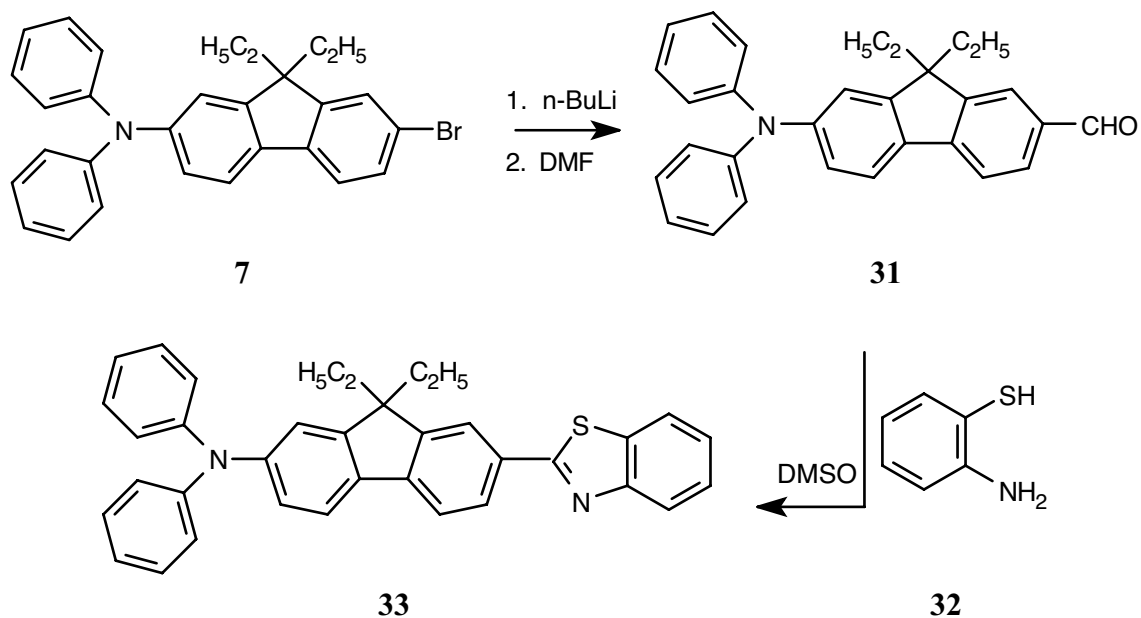
A third type of chromophore was designed to have an increased conjugation length via the incorporation of a second fluorene group in the  $\pi$ -electron bridging unit.<sup>8</sup> Compound **7** was converted to the tri-n-butyltin derivative **29**. Compound **29** reacts with **16** under palladium catalyzed Stille conditions to yield 4-(9,9,9',9'-tetraethyl-7'-(diphenylamino)-2',7'-bifluoren-2-yl)vinyl)pyridine **30**. Increasing the conjugation length by incorporation of the second fluorene ring system into the bridging unit reduces the effective two-photon absorption cross section, as seen in **Table 1**. This may be due to a decrease in the effective conjugation between the donor and the acceptor groups. This

molecular design increases the rotation of the adjacent fluorene groups and ultimately decreases the planarity of the chromophore.



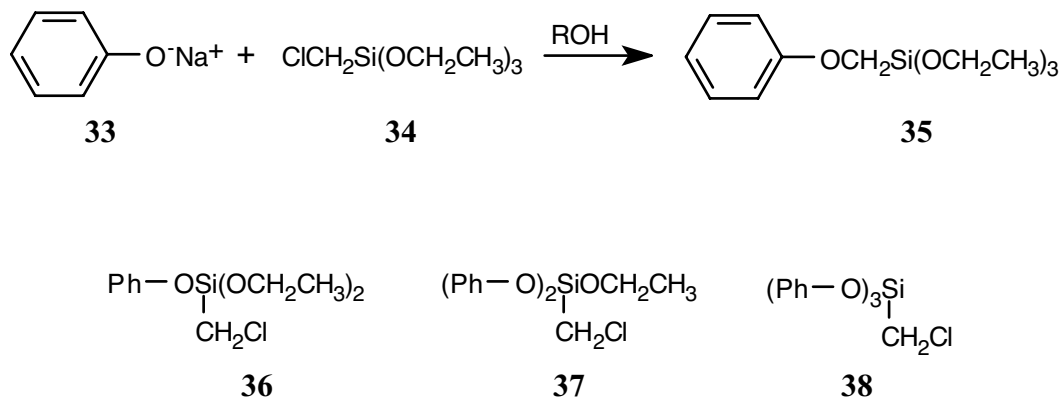
Benzothiazole can be used in place of vinyl pyridine for the heterocyclic  $\pi$ -acceptor group for compounds containing the fluorene bridge.<sup>9</sup> Synthesis of benzothiazole derivatives is easier since the Heck addition of the vinyl-pyridine acceptor group is eliminated. Benzothiazole compounds can be synthesized by reacting N,N-diphenyl-7-bromo-9,9-diethyl-9H-fluorene-2-amine **7** with butyl lithium and then DMF to yield 7-diphenylamino-9,9-diethylfluorene-2-carboxaldehyde **31**. Compound **31** was reacted 2-aminothiophenol **32** in DMSO to yield 9,9-diethyl-(7-benzothiazol-2-ylfluorene-2-yl)diphenylamine **33**. The benzothiazole substituent is a good alternative to vinyl pyridine. There are not any severe changes in the effective two-photon absorption coefficients (**Table 1**). For instance, the fluorene bridged compound **17** with the vinyl-pyridine acceptor has an effective two-photon cross section,  $\sigma_2'$ , of  $97.0 \text{ cm}^4 \cdot \text{sec/ph} \cdot$

molecule and the same compound with the benzothiazole unit acceptor **33** has an effective two-photon cross section of  $97.5 \text{ cm}^4 \cdot \text{sec/ph} \cdot \text{molecule}.$ <sup>9</sup>



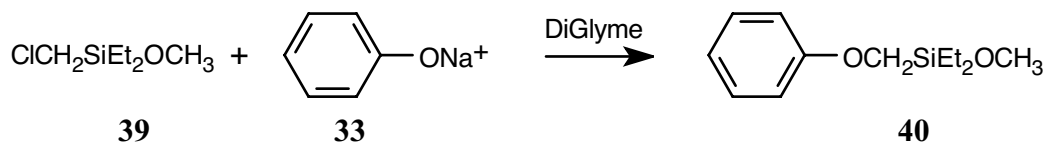
### Trialkoxy(aryloxyalkyl)silane Formation

The formation of a carbon-oxygen bond of the type  $\text{ArO}(\text{CH}_2)_n\text{SiX}_3$  ( $\text{X} = \text{alkyl}$  and alkoxy) for trialky(aryloxyalkyl)silanes and trialkoxy(aryloxyalkyl)silanes is problematic. The replacement of the chlorine atom in trialkoxy(chloromethyl)silanes **34**

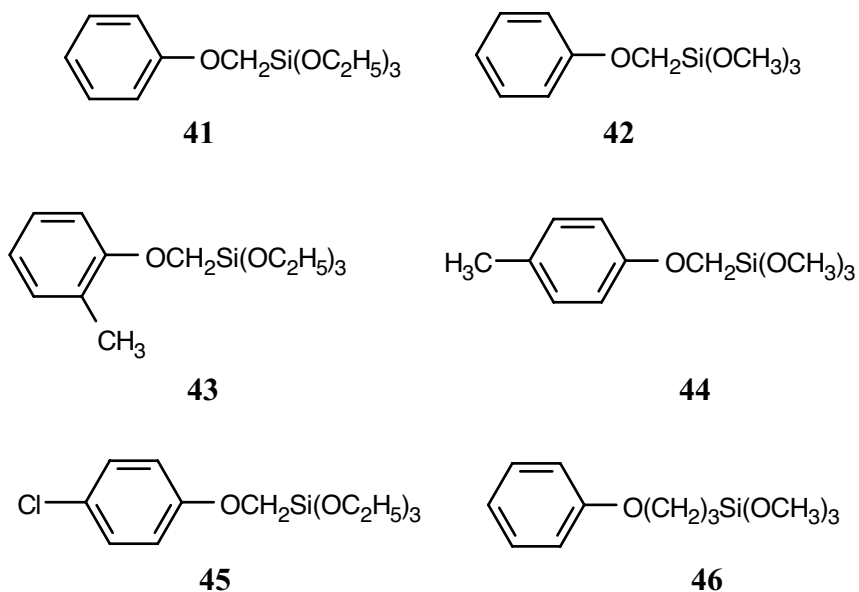


by a phenoxy group by the reaction with sodium phenoxide **33** in an alcohol medium is not successful because of the occurrence of cleavage of the Si-C bond and alcoholysis as illustrated by compounds **36**, **37** and **38**.<sup>10</sup>

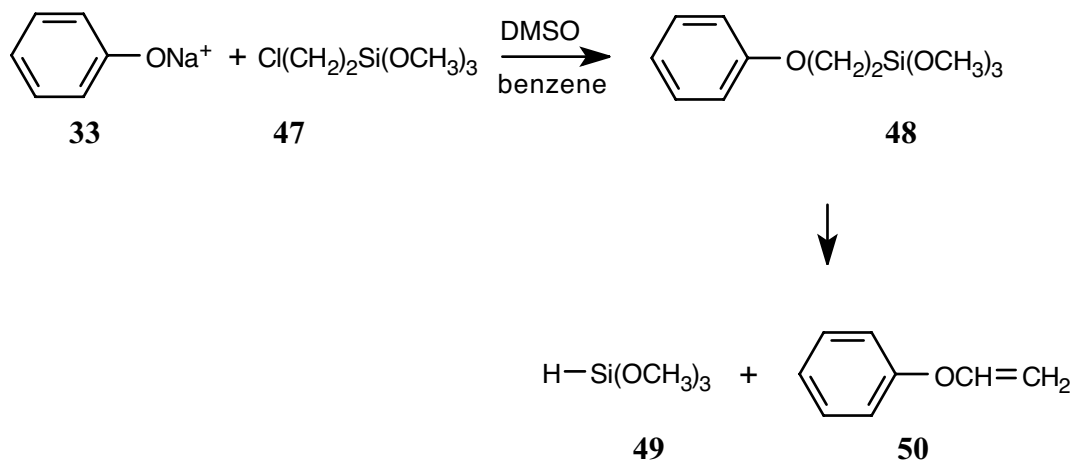
The reaction of (chloromethyl)diethylmethoxysilane **39** with sodium phenoxide **33** in diglyme yields diethylmethoxy(phenoxyethyl)silane **40**.<sup>11</sup> Hydrolysis of the single alkoxy function does not lead to a network in this case.



A more recent method<sup>10</sup> for the synthesis of the trialkoxy(aryloxyalkyl)silanes [ $\text{YC}_6\text{H}_4\text{O}(\text{CH}_2)\text{Si}(\text{OR})_3$  with  $n = 1, 3$ ] involves the reaction of trialkoxychloroalkylsilane derivatives with sodium or potassium phenoxide in a mixture of benzene and dimethyl sulfoxide (DMSO). As the DMSO concentration increases from 20 to 100 percent, the reaction time decreases from 12 hour to 5 hours, respectively, indicating a rate increase based on solvent polarity. Compounds **41** – **46** were synthesized by this method.

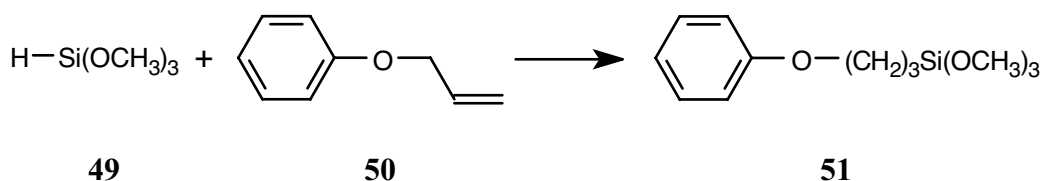


A limitation of this method is the failure of chloroethyl silane derivatives to form stable trialkoxy(2-aryloxyethyl)silanes ( $n = 2$ ) because of “ $\beta$  breakdown.”<sup>10</sup> Thus,



sodium phenoxide **33** reacts with chloroethyltrimethoxysilane **47** to yield the corresponding phenoxyethyltrimethoxysilane **48** which subsequently loses trimethoxysilane **49** yielding phenyl vinyl ether **50**. The phenoxyethyl compounds essentially undergo a reverse hydrosilation. Interestingly, the chemical shifts for silicon-29 remained the same for the entire series of compounds synthesized ( $\delta$  -53.9 ppm).<sup>12</sup>

The addition of triethoxysilane **49** to allyl phenyl ether **51** proceeds without complication and leads to triethoxy(3-phenoxypropyl)silane **51**.<sup>13</sup>



## EXPERIMENTAL

### Instrumentation and Chemicals

An Electrothermal capillary melting point apparatus equipped with a thermocouple was used to obtain melting points. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC-200 spectrometer ( $^1\text{H}$  and  $^{13}\text{C}$ ), with tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded with a Perkin Elmer 1600 Series FTIR spectrometer using KBr pellets. Elemental analysis and mass spectrometry were done by Materials Laboratory Sample Analysis (MLSA). All reagents were purchased from Aldrich Chemical Company and used without further purification.

### 2,7-Dibromofluorene **53**

A mixture of fluorene (157.5 g, 0.95 mol) and iodine (2.69 g, 0.011 mol) in methylene chloride (1L) was mechanically stirred at room temperature. A solution of bromine (100 mL, 1.941 mol) in methylene chloride (150 mL) was added dropwise over 2 h resulting in a red solution. A bicarbonate solution (8 g  $\text{NaHCO}_3$ , 250 mL  $\text{H}_2\text{O}$ ) was added and the mixture was stirred overnight. Methylene chloride was removed, water was slowly added (750 mL) and a creamy white precipitate formed. This mixture was cooled to 40 °C in a water bath and the precipitate was filtered and washed with water (3 L) to afford **53** (304 g, 99%) as white crystals: mp 156-159.3 °C; IR (KBr)  $\text{cm}^{-1}$  2919 (C-H), 1453 and 1396 (Ar-C=C), 813 (C-H out-of-plane);  $^1\text{H}$  NMR  $\delta$  3.817 (s, 2H,  $\text{CH}_2$ ), 7.847

(m, 2H, Ar-H), 7.543 (s, 2H, Ar-H), 7.627 (d, 2H, Ar-H);  $^{13}\text{C}$  NMR ppm 36.76, 76.58, 77.23, 77.85, 121.08, 121.34, 128.44, 130.26, 139.83, 144.92; mass spectrum,  $m/z$  (relative intensity) 326, 324, 322 ( $\text{M}^+$ , 43.6, 100, 48.4), 245, 243 (75.1, 78.6), 164 (24.6), 163 (42), 82 (5.6). Anal. Calcd for  $\text{C}_{13}\text{H}_8\text{Br}_2$ : C, 48.16; H, 2.49; Br, 49.34. Found C, 48.08; H, 2.18; Br, 49.51.

### **2,7-dibromo-9,9-diethylfluorene 3**

A mixture of 2,7-dibromofluorene (66.5 g, 0.205 mol), potassium iodide (3.4 g) and potassium hydroxide (56 g, 1 mol) in dimethyl sulfoxide (150 mL) was cooled to 10 °C. A solution of ethyl iodide (39 mL) was added dropwise over 45 min in order to maintain the internal temperature in a range of 5-10 °C. The solution was mechanically stirred at room temperature for 24 h and poured into water. A purplish precipitate was filtered and recrystallized from hexanes (550 mL, charcoal) to afford **3** (65.4 g, 84%) as cream-colored crystals: mp 153-155 °C; IR (KBr)  $\text{cm}^{-1}$  3070 (Ar-C-H), 1572 and 1449 (Ar-C=C), 2960, 2916 and 2871 (C-H), 814 (C-H out-of-plane);  $^1\text{H}$  NMR  $\delta$  0.306 (t, 6H,  $\text{CH}_3$ ), 2.00 (q, 4H,  $\text{CH}_2$ ), 7.44-7.50 (m, 6H, Ar-H);  $^{13}\text{C}$  NMR ppm 8.74, 32.36, 32.43, 32.50, 32.83, 56.92, 121.27, 121.67, 126.43, 130.36, 139.61, 151.872; mass spectrum,  $m/z$  (relative intensity) 382, 380, 378 ( $\text{M}^+$ , 62.1, 100, 49.3), 353, 351, 349 (18.42, 41.8, 19.7), 272, 270 (41.4, 42.3), 191, 189 (12.9, 11.9), 176 (6.5). Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{Br}_2$ : C, 53.69; H 4.24; Br, 42.06. Found: C, 53.73; H, 4.21; Br, 42.44.



## 2-Bromo-7-formyl-9,9-diethylfluorene 54

A solution of 2,7-dibromo-9,9-diethylfluorene (57.7 g, 0.15 mol) in THF (260 mL) was cooled to  $-68\text{ }^{\circ}\text{C}$ . A solution of n-butyllithium in hexanes (1.6 M, 100 mL) was added dropwise in order to maintain the internal temperature at  $-70\text{ }^{\circ}\text{C}$ . The clear yellow solution was stirred for 20 min and dimethylformamide (20 mL) in THF (25 mL) was added dropwise over 5 min. The solution was stirred for 1 h, warmed to  $5\text{ }^{\circ}\text{C}$ , a 3:1 water: hydrochloric acid solution was added (10 min), and finally stirred overnight while warming to room temperature. The solution was diluted with toluene (200 mL) and the organic layer was separated, washed twice with a saturated sodium bicarbonate solution, dried over  $\text{MgSO}_4$  and evaporated. Solvent removal resulted in a yellow solid which was washed with cold hexanes, filtered and recrystallized from heptane (100 mL) to afford **3** (49.97 g, 82.4%) as white crystals: mp  $123\text{--}128\text{ }^{\circ}\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$  2960 and 2962 (C-H), 2857 and 2813 (aldehydic C-H), 1688 (C=O);  $^1\text{H}$  NMR  $\delta$  0.30 (t, 6H,  $\text{CH}_3$ ), 2.040 (m, 4H,  $\text{CH}_2$ ), 7.51–7.86 (m, 6 H, Ar-H), 10.07 (s, 1H, CHO);  $^{13}\text{C}$  NMR ppm 8.42, 8.57, 8.75, 8.86, 32.77, 56.85, 120.24, 122.35, 123.29, 123.51, 126.72, 130.75, 135.78, 139.09, 146.87, 150.48, 153.57, 192.25. mass spectrum,  $m/z$  (relative intensity) 330, 328 ( $\text{M}^+$ , 37.5, 37.3), 301, 299 (27.2, 28.5), 272 (10.7), 192 (100)). Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{BrNS}$ : C, 66.19; H, 4.86; N, 3.22. Found C, 66.27; H, 4.81; N, 3.13.

## 2-(7-Bromo-9,9-diethyl-2-fluorenyl)benzothiazole 55

A mixture of 2-bromo-7-formyl-9,9-diethylfluorene (40 g, 0.122 mol) and 2-aminothiophenol (18 mL) in DMSO (61 mL) was heated to  $185\text{ }^{\circ}\text{C}$  for 1 h. The reaction mixture was poured into a solution containing sodium chloride (150 g), water (600 mL)

and crushed ice (600 g) resulting in a pale green precipitate. The solution was stirred overnight (20 h) and filtered. The crude product was slurried in ethanol (400 mL), filtered and recrystallized from heptane (500 mL) to afford **55** (45 g, 85%) as yellow crystals: mp 132-134.8 °C; IR (KBr)  $\text{cm}^{-1}$  3059 (Ar-H), 2962, 2921, and 2374 (C-H), 1283 (C-N);  $^1\text{H}$  NMR 0.34 (t, 6H,  $\text{CH}_3$ ), 2.05 (m, 4H,  $\text{CH}_2$ ), 7.37-8.1 (m, 10H, Ar-H);  $^{13}\text{C}$  NMR ppm 8.53, 8.64, 8.72, 8.79, 32.88, 57.04, 69.26, 69.33, 121.77, 126.57, 130.43, 132.57, 134.87, 139.60, 143.71, 150.58, 152.99, 153.90, 168.63. mass spectrum,  $m/z$  (relative intensity) 435, 433 ( $\text{M}^+$ , 94.4, 100), 406, 404 (65.9, 66.3), 325 (97.6), 310 (21.4), 162.5 (39.3).  
Anal. Calcd for  $\text{C}_{18}\text{H}_{17}\text{BrO}$  : C, 65.65; H, 5.21. Found C, 63.99; H, 5.23.

### 3-Benzoyloxydiphenylamine **57**

A solution containing 3-hydroxydiphenylamine (18.51 g, 0.1 mol) and potassium carbonate (27.63 g, 0.2 mol) in dimethylformamide (100 mL) was cooled to 10 °C under a nitrogen atmosphere. A solution of benzyl bromide (13 mL, 0.11 mol) was added dropwise over 30 min and the solution stirred overnight (20 h). The reaction mixture was poured into water (250 mL) resulting in a brown precipitate. The solution was diluted with toluene (200 mL) and the organic layer was separated, washed with water and dried over  $\text{MgSO}_4$ . The crude product (27 g) was chromatographed on silica using a heptane: toluene (3:1 ; 2:1; 1:1) solution as eluent to afford **57** (24.22 g, 88%) as white crystals: mp 51-54 °C; IR (KBr)  $\text{cm}^{-1}$  3026 (Ar-C-H), 2921 and 2850 (C-H), 1594 and 1493 (Ar-C=C);  $^1\text{H}$  NMR  $\delta$  1.01 (s, 2H, N-H), 5.03 (s, 2H,  $\text{OCH}_2\text{-Ar}$ ), 6.55-7.60 (m, 14H, Ar-H);  $^{13}\text{C}$  NMR ppm 70.06, 104.45, 107.69, 110.78, 118.72, 121.78, 127.02, 127.60, 128.04,

128.69, 129.49, 130.26, 131.60, 137.10, 142.52, 144.38, 159.92; MS 275 (275). Anal. Calcd for C<sub>18</sub>H<sub>17</sub> NO: C, 82.86; H, 6.23; N, 5.09. Found: C, 82.76; H, 6.22; N, 5.03.

### **Palladium Catalyst<sup>P1</sup> (Pd(dba)<sub>2</sub>)**

A mixture of sodium acetate (8.1098 g), dibenzylidene acetone (9.4698 g), and methanol (200 mL) was heated to reflux and stirred for 30 min. Palladium chloride (2.1932 g) was added and the hot mixture was stirred for 4 h, resulting in a reddish-purple precipitate. The mixture was cooled to room temperature, filtered, washed with acetone and water and dried under vacuum (24 h).

### **2-(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole<sup>14</sup> 58**

A mixture of 3-hydroxydiphenylamine (12.5 g, 0.045 mol), 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole (16.5 g, 0.038 mol) and toluene (300 mL) was distilled and cooled to room temperature. A combination of Pd(dba)<sub>2</sub> (0.4304 g), dppf (diphenylphosphinoferrocene) (0.3938 g) and sodium t-butoxide (5.39 g) were added to the solution and it was heated at 85°C overnight (20h). Toluene was added, the organic layer was separated and washed with a saturated solution of sodium chloride and dried with MgSO<sub>4</sub>. After evaporation of toluene, the crude product was chromatographed on silica using toluene as eluent and recrystallized from 1:5 toluene:heptane solution (300 mL) to afford **58** (21.7 g, 91.2%) as pale yellow crystals: mp 181-183 °C; IR (KBr) cm<sup>-1</sup> 3031 (Ar-C-H), 2961 and 2918 (C-H), 1592 and 1487 (Ar-C=C), 1275 (C-N), 1218 (C-O); 0.38 (t, 6H, CH<sub>3</sub>), 1.85-2.21 (m, 4H, CH<sub>2</sub>), 4.94 (s, 1H, OH), 6.63-8.19 (m, 24H, Ar-H); <sup>13</sup>C NMR ppm 32.87, 56.67, 70.10, 110.57, 116.68, 119.16, 119.34, 119.41, 119.56,

121.27, 121.41, 121.52, 121.74, 122.87, 123.09, 123.23, 123.41, 123.67, 124.65, 125.31, 126.62, 127.63, 128.07, 128.36, 128.69, 129.42, 130.00, 131.02, 134.59, 139.50, 136.95, 194.96, 147.72, 148.20, 149.18, 150.93, 152.27, 153.51, 159.77, 169.20; mass spectrum,  $m/z$  (relative intensity) 628 ( $M^+$ ), 537 (4.0), 508 (3.9), 493 (7.6), 479 (4.4). Anal. Calcd for  $C_{43}H_{36}N_2OS$ : C, 82.12; H, 5.78; N, 4.46; S, 5.10. Found: C, 81.06; H, 5.82; N, 4.37; S, 5.08.

### **2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **59****

A mixture of 2-(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole (10 g, 0.19 mol) and pyridine hydrochloride (85 g, 0.74 mol) was heated<sup>15</sup> to 200 °C for 1.5 h. The solution was poured into warm water, stirred for 30 min and filtered. A slurry of the red precipitate and a dilute ammonium hydroxide solution (5 %) was stirred overnight (20 h), filtered, and the residue was recrystallized from toluene (1500 mL, charcoal) to afford **59** (6.8g, 80%) as bright yellow crystals: mp 248-250 °C; IR  $cm^{-1}$  3434 (OH), 3026 (Ar-C-H), 2921 (C-H); mass spectrum,  $m/z$  538 ( $M^+$ , 100), 509 (3.7), 494 (4.4), 269 (0.3). Anal. Calcd for  $C_{36}H_{30}N_2OS$ : C, 80.29; H, 5.57; N, 5.20; S, 5.95. Found: C, 80.75; H, 5.82; S, 6.01.

### **2-(7-(3-triethoxysiloxymethyldiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole<sup>10</sup> **60****

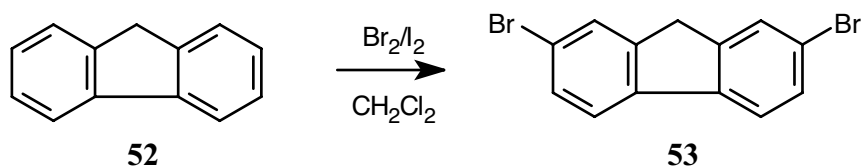
A mixture of 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole (4 g, 0.0074 mol), dimethylsulfoxide (18 mL), and toluene (70 mL) was refluxed, distilled (to remove water/toluene) under a nitrogen atmosphere and cooled to room temperature. Potassium t-butoxide (0.9168 g, 0.0082 mol) was added to

the green solution, distilled and cooled to room temperature. A solution of chloromethyltriethoxysilane (1.7 mL, 0.0082 mol) was added dropwise over 5 min to the mixture and heated to 85 °C for 20 h. The mixture was cooled to room temperature and solvent was removed in vacuo. The yellow residue was dissolve in dry hexanes and distilled to yield **60** as a yellow oil. Mass spectrum,  $m/z$  852(28), 714 ( $M^+$ , 100), 704 (14), 538 (19).

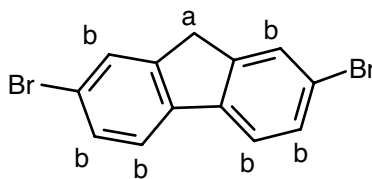
## RESULTS AND DISCUSSION

### 2,7-Dibromofluorene

Bromination of fluorene **52** involved an electrophilic substitution with bromine using iodine as a catalyst. The infrared spectrum of 2,7-dibromofluorene **53** is shown in **Figure 16**. As expected, the IR contains absorptions attributable to aliphatic C-H stretching at  $2919\text{ cm}^{-1}$  and aromatic C=C stretching at  $1598$  and  $1453\text{ cm}^{-1}$ . The mass

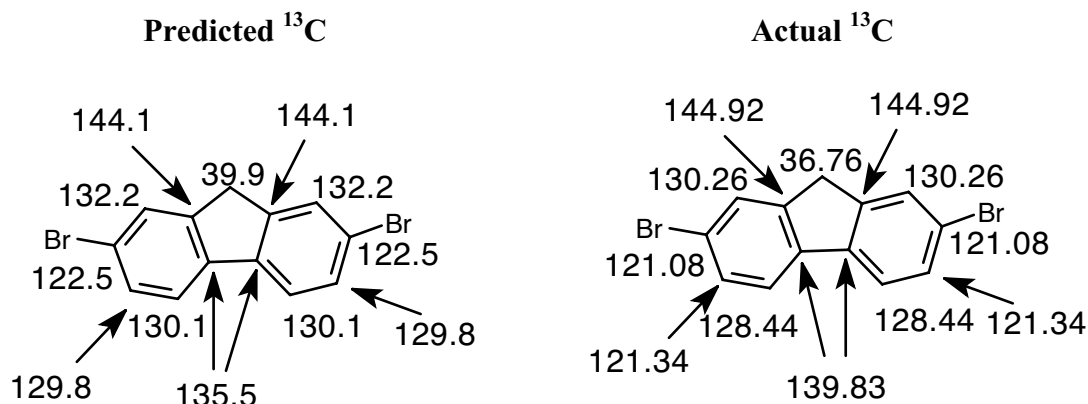


spectrum displays the presence of two bromines with the three distinct peaks at 322, 324, and 326 (M, M+2, M+4). The  $^1\text{H}$  NMR spectrum (**Figure 17**) of 2,7-dibromofluorene **53** exhibits 1) a singlet at  $3.817\text{ }\delta$  attributable to two aliphatic hydrogens labeled a in **Figure 3**, 2) a multiplet between  $7.62\text{--}7.85\text{ }\delta$  attributable to six aromatic hydrogens labeled b in **Figure 3**. A peak at  $4.89\text{ }\delta$  in the  $^1\text{H}$  NMR spectrum can be attributed to an impurity because **53** was not purified. The  $^{13}\text{C}$  NMR (**Figure 18**) spectrum of **53**



**Figure 3.**  $^1\text{H}$  NMR assignments for 2,7-dibromofluorene **53**.

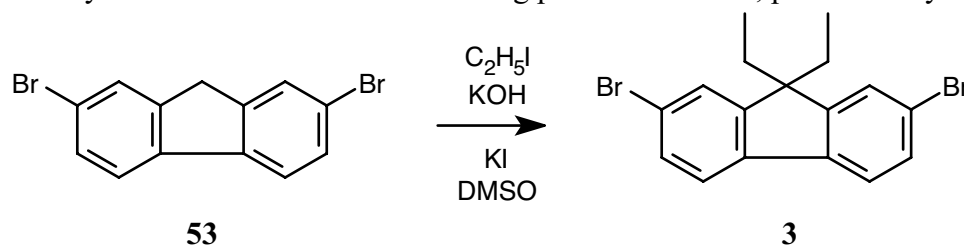
exhibits eight unique carbon absorptions. A comparison of the predicted  $^{13}\text{C}$  and the actual  $^{13}\text{C}$  absorptions of 2,7-dibromofluorene **53** is shown in **Figure 4**.



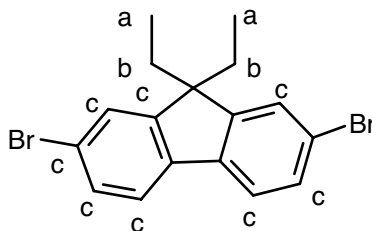
**Figure 4.**  $^{13}\text{C}$  NMR Assignments for 2,7-dibromofluorene **53**.

### 2,7-dibromo-9,9-diethylfluorene

Alkylation of **53** was carried out using potassium iodide, potassium hydroxide



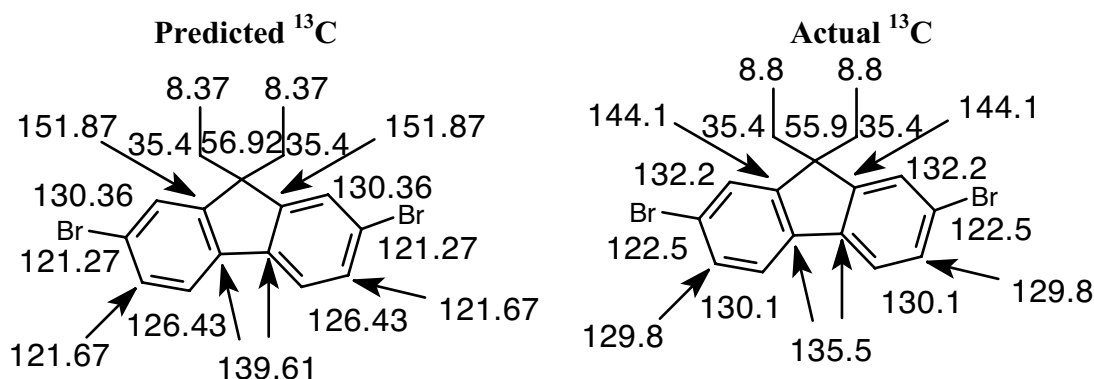
and ethyl iodide in DMSO. The infrared spectrum of 2,7-dibromo-9,9-diethylfluorene **3** is shown in **Figure 19**. As expected, the IR contains absorptions attributable to aromatic C-H



**Figure 5.**  $^1\text{H}$  NMR assignments for 9,9-diethyl-2,7-dibromofluorene **3**.

bending at  $3070\text{ cm}^{-1}$ , aliphatic C-H bending at  $2960$ ,  $2916$ , and  $2871\text{ cm}^{-1}$ , and aromatic C=C bending at  $1572$  and  $1449\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum (**Figure 20**) for **3** exhibits 1) an triplet at  $0.31\text{ }\delta$  representing six aliphatic hydrogens labeled a in **Figure 5**, 2) an

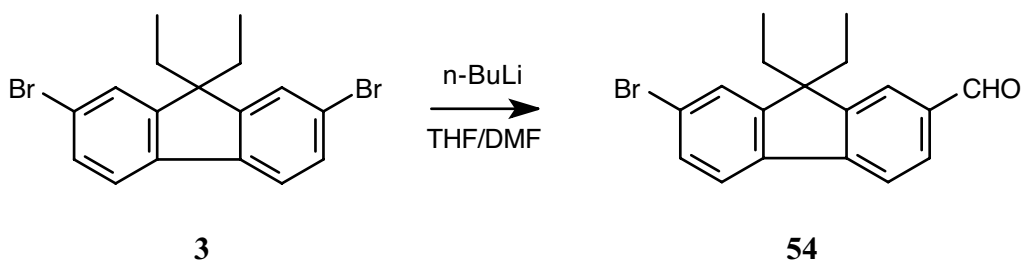
quartet at 2.00  $\delta$  representing four aliphatic hydrogens labeled b in **Figure 5**, and 3) an multiplet between 7.44-7.50 representing six aromatic hydrogens labeled c in **Figure 5**. The observed  $^{13}\text{C}$  NMR (**Figure 21**) spectrum of **3** exhibits seventeen unique carbon absorptions. A comparison of the predicted  $^{13}\text{C}$  and the actual  $^{13}\text{C}$  absorptions of **3** is shown in **Figure 6**.



**Figure 6.**  $^{13}\text{C}$  NMR Assignments for 9,9-diethyl-2,7-dibromofluorene **3**.

### 2-bromo-7-formyl-9,9-diethylfluorene

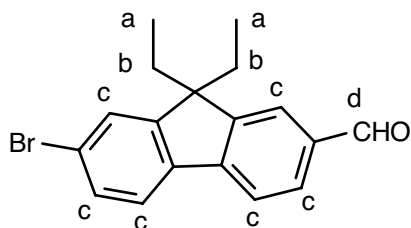
The synthesis of 2-bromo-7-formyl-9,9-diethylfluorene **54** involved a reaction of **3** with butyllithium followed by a reaction of the organolithium with dimethylformamide



(DMF). The infrared spectrum of 2-bromo-7-formyl-9,9-diethylfluorene **54** is shown in **Figure 22**. The IR spectrum contain absorptions attributable to the aliphatic C-H bending at 2962 and 2960  $\text{cm}^{-1}$ , the aldehydic C-H bending at 2857 and 2813  $\text{cm}^{-1}$ , and an

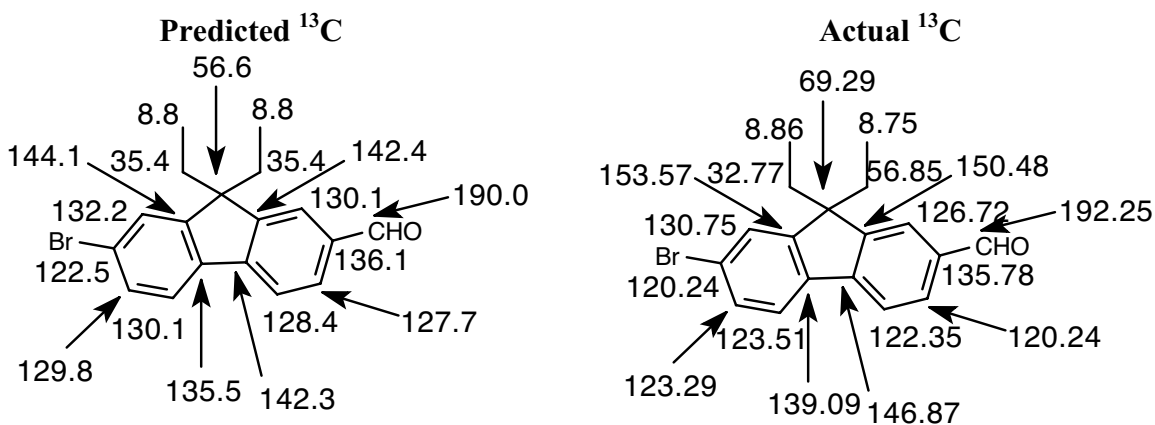


aldehyde carbonyl absorption at  $1688\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum (**Figure 23**) of 2-bromo-7-formyl-9,9-diethylfluorene **54** exhibits 1) a triplet at  $0.34\text{ }\delta$  representing



**Figure 7.**  $^1\text{H}$  NMR Assignments for 2-bromo-7-formyl-9,9-diethylfluorene **54**.

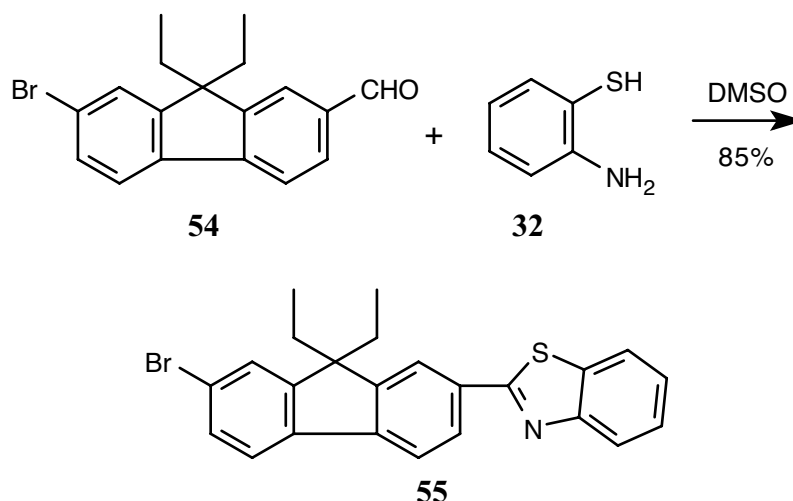
six aliphatic hydrogens labeled a in **Figure 7**, 2) a quartet at  $2.04\text{ }\delta$  representing four hydrogens labeled b in **Figure 7**, 3) a multiplet between  $7.51\text{--}7.86\text{ }\delta$  represents six hydrogens labeled c in **Figure 7** and 4) a singlet at  $10.07\text{ }\delta$  representing an aldehydic proton labeled d in **Figure 7**. The  $^{13}\text{C}$  NMR (**Figure 24**) spectrum of **54** exhibits twenty-one unique carbon absorptions. A comparison of the predicted  $^{13}\text{C}$  and the actual  $^{13}\text{C}$  absorptions of **54** is shown in **Figure 8**.



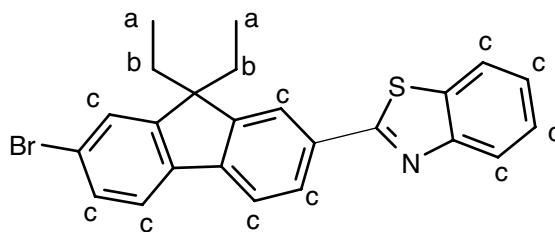
**Figure 8.**  $^{13}\text{C}$  NMR Assignments for 2-bromo-7-formyl-9,9-diethylfluorene **54**.

## 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole

The conversion of 2-bromo-7-formyl-9,9-diethylfluorene **54** to 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55** involved use of 2-aminothiophenol **32** in DMSO. The infrared spectrum of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55** is shown in **Figure 25**. As expected, the IR spectrum contains absorptions attributable to aromatic C-H stretching at 3059  $\text{cm}^{-1}$ , aliphatic C-H stretching at 2962, 2921, and 2374  $\text{cm}^{-1}$ , and C-N stretching at 1283  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum (**Figure 26**) exhibits 1) a triplet at

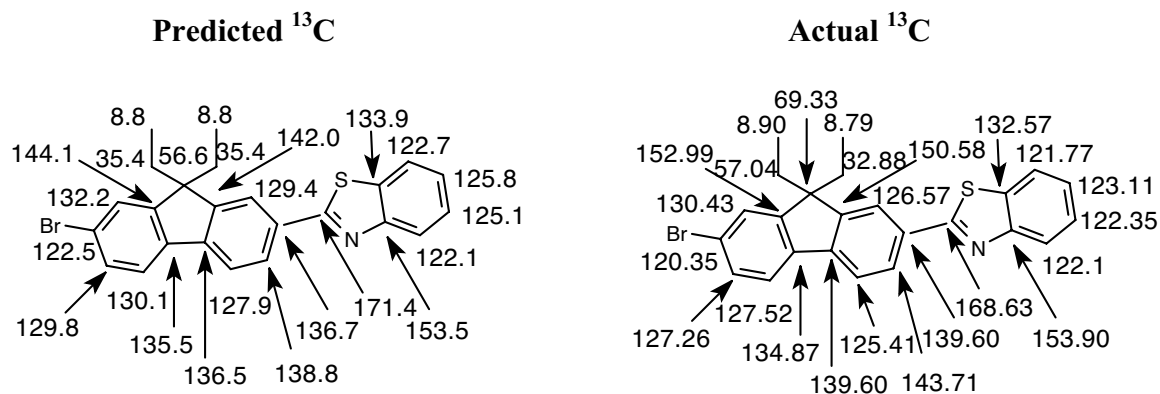


0.34  $\delta$  representing six hydrogens labeled a in **Figure 9**, 2) a quartet at 2.05  $\delta$  representing four hydrogens labeled b in **Figure 9**, and 3) a multiplet between 7.37-8.1  $\delta$  representing ten hydrogens labeled c in **Figure 9**. The  $^{13}\text{C}$  NMR (**Figure 27**) spectrum of



**Figure 9.**  $^1\text{H}$  NMR assignments for 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55**.

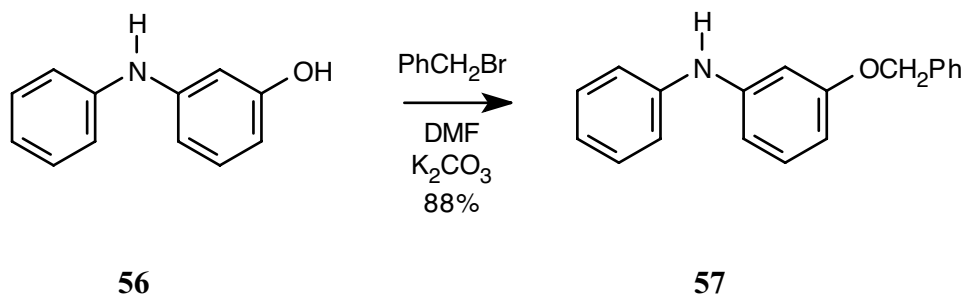
**55** exhibits twenty-five unique carbon absorptions. A comparison of the predicted  $^{13}\text{C}$  and the actual  $^{13}\text{C}$  absorptions of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55** is shown in **Figure 10**.



**Figure 10.**  $^{13}\text{C}$  NMR Assignments for 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55**.

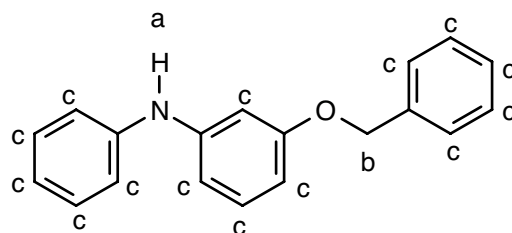
### 3-benzyloxydiphenylamine

The alkylation of 3-hydroxydiphenylamine **56** involved a reaction with benzyl bromide and potassium carbonate in DMF yielding 3-benzyloxydiphenylamine **57**. The infrared spectrum of **57** is shown in **Figure 28**. The IR contains absorptions

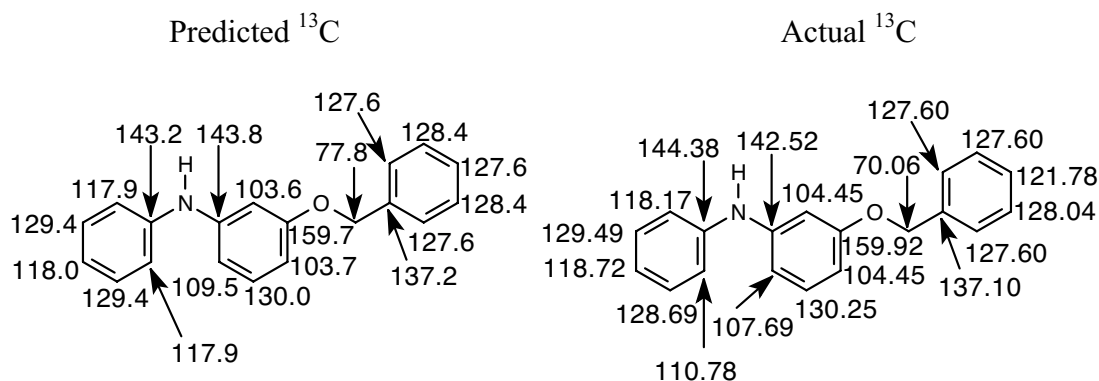


attributable to aromatic C-H bending at  $3026\text{ cm}^{-1}$ , aliphatic C-H bending at  $2921$  and  $2850\text{ cm}^{-1}$ , and aromatic C=C bending at  $1594$  and  $1493\text{ cm}^{-1}$  are observed. The  $^1\text{H}$  NMR spectrum (**Figure 29**) of **57** exhibits 1) a singlet at  $1.61\text{ }\delta$  representing one amine

hydrogen labeled a in **Figure 11**, 2) a singlet at 5.03  $\delta$  representing two aliphatic hydrogens labeled b in **Figure 11**, and 3) a multiplet at 6.55-7.60  $\delta$  representing fourteen aromatic hydrogens labeled c in **Figure 11**. The  $^{13}\text{C}$  NMR (**Figure 30**) spectrum exhibits nineteen unique carbons. A comparison of the predicted  $^{13}\text{C}$  and the actual  $^{13}\text{C}$  absorptions of 3-benzyloxidiphenylamine **57** is shown in **Figure 12**.



**Figure 11.**  $^1\text{H}$  NMR assignments for 3-benzyloxidiphenylamine **57**.



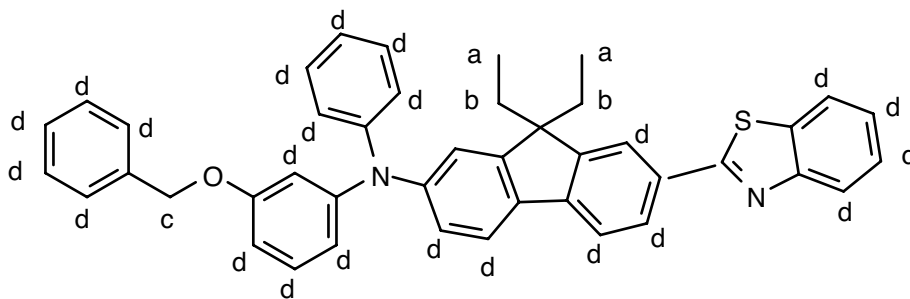
**Figure 12.**  $^{13}\text{C}$  assignments for 3-benzyloxidiphenylamine **57**

## 2-(7-(3-benzyloxidiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole

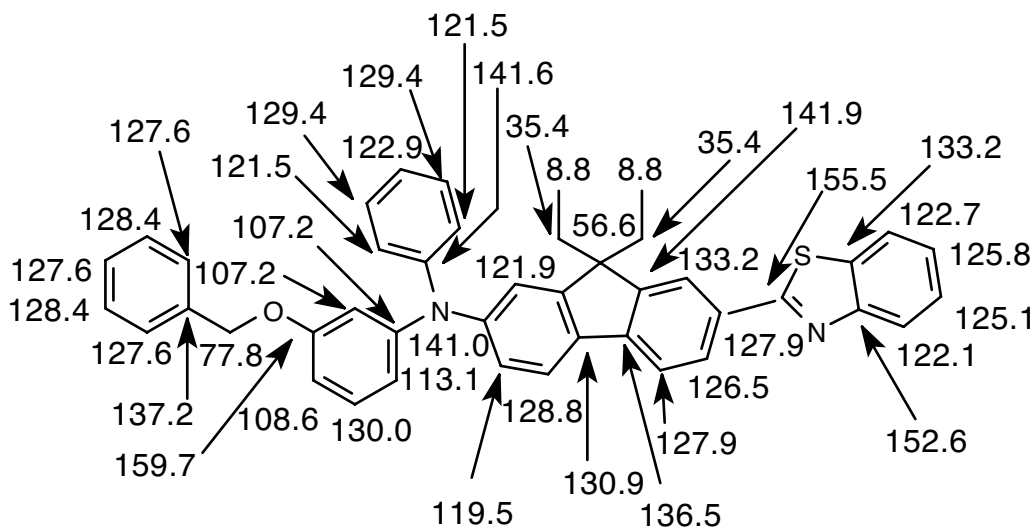
The palladium catalyzed coupling of 3-benzyloxidiphenylamine **57** with 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55** yielded 2-(7-(3-benzyloxidiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58** in excellent yield. The procedure deviated from the literature procedure as indicated in **Table 2**. The infrared spectrum of 2-(7-(3-benzyloxidiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58** is shown in



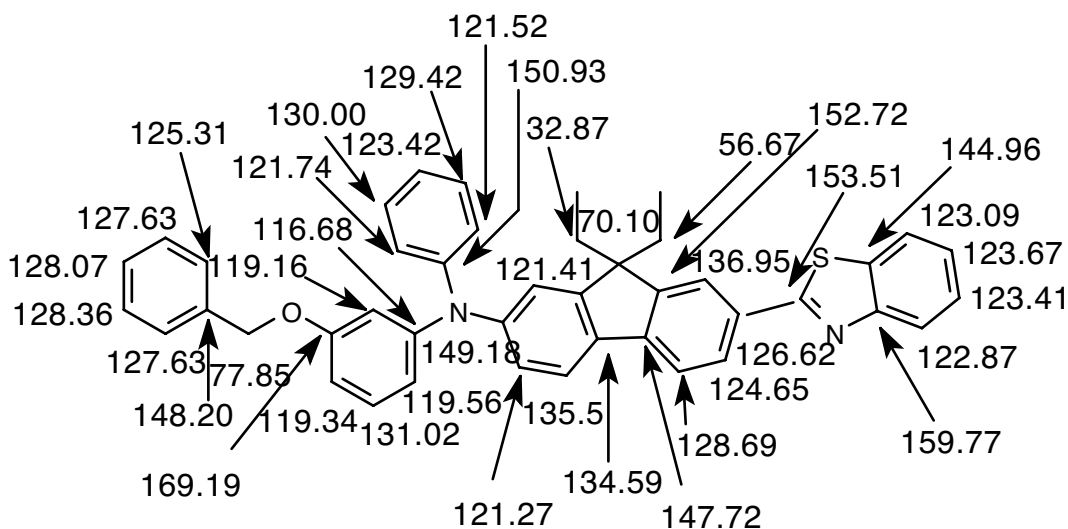
respectively.



**Figure 13.**  $^1\text{H}$  assignments for **58**.



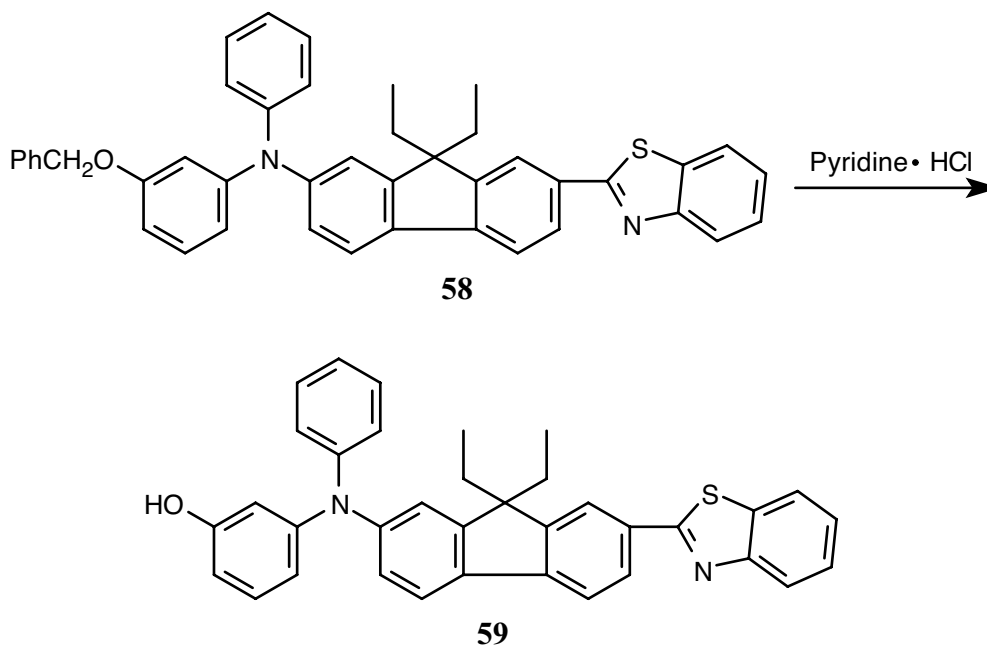
**Figure 14.** Predicted  $^{13}\text{C}$  absorptions of **58**.



**Figure 15.** Actual  $^{13}\text{C}$  absorptions **58**.

### 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-fluorenyl)benzothiazole

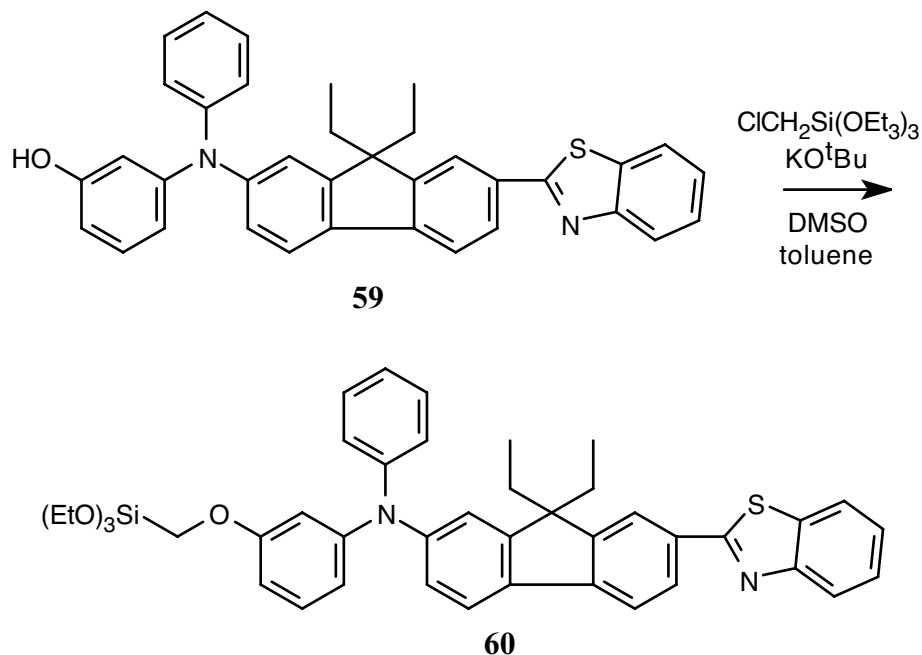
The removal of the benzyl protective group from 2-(7-(3-benzyloxy-diphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58** using pyridine hydrochloride yielded 2-(7-(3-hydroxydiphenylamino)-9,9-diethylfluorenyl)benzothiazole **59**.



The infrared spectrum for 2-(7-(3-hydroxydiphenylamino)-9,9-diethylfluorenyl)benzothiazole **59** is shown in **Figure 34**. The IR attributable to aromatic O-H stretching at  $3434\text{ cm}^{-1}$ , aromatic C-H stretching at  $3026\text{ cm}^{-1}$ , and aliphatic C-H stretching at  $2921\text{ cm}^{-1}$ . Because of the low solubility of the compound, a  $^1\text{H}$  NMR and a  $^{13}\text{C}$  NMR could not be done.

### 2-(7-(3-triethoxysilyloxymethylphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole

The compound, 2-(7-(3-hydroxydiphenylamino)-9,9-diethylfluorenyl)benzothiazole **59** was reacted with chloromethyltriethoxysilane and potassium t-butoxide to yield 2-(7-(3-(triethoxysilyloxymethoxyphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **60**. The procedure deviated from the literature procedure as indicated in **Table 3**.





**Table 3.** Silane Modifications

	<i>Current Work</i>	<i>Literature</i>
<i>Solvent</i>	Toluene	Benzene
<i>Atmosphere</i>	N <sub>2</sub>	<i>No N</i>
<i>Temperature</i>	85 °C	Not indicated
<i>Reaction Time</i>	overnight	12 H

Due to potential decomposition of the product, nitrogen was used as a reaction atmosphere and all glassware was dried in an oven overnight. Fractional distillation could not be used for purification because the product was of such high molecular weight. Once the DMSO and toluene were removed via vacuum distillation, dried hexanes were added to the residue in an attempt to dissolve and remove product. The residue that remained after the hexanes were removed was miniscule. A <sup>1</sup>H NMR (**Figure 35**) was obtained and did not conclusively demonstrate that the desired product was prepared. An electron-impact mass spectrum does show the mass ion peak along with other peaks as well. There was no conclusive evidence showing that the product was isolated or purified.

### Conclusions and Future Work

- The addition of the benzyl protective group to 3-hydroxydiphenylamine provided 3-benzyloxydiphenylamine.
- Two new compounds: 2-(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58** and 2-(7-(3-hydroxydiphenylamino)-9,9-diethylfluorenyl)benzothiazole **59**, were successfully synthesized and characterized.
- There was no conclusive evidence showing 2-(7-(3-(triethoxysilyloxymethoxy)phenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **60** was isolated or purified.

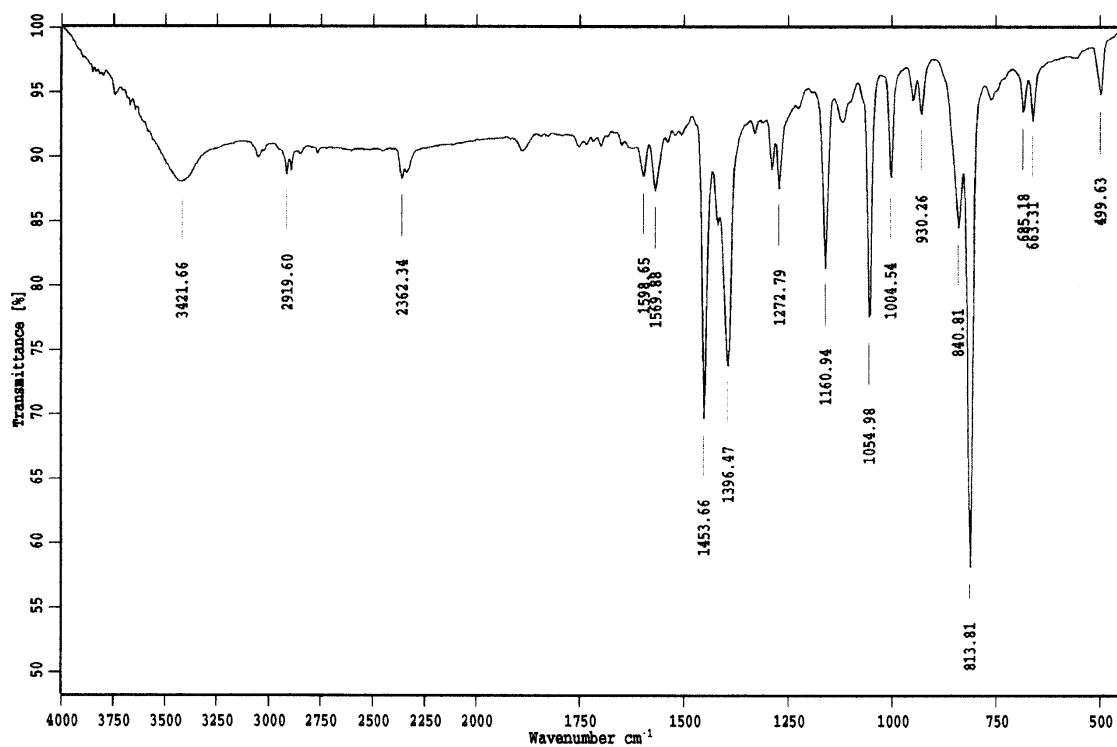


Figure 16. IR spectrum of 2,7-Dibromofluorene **53**.

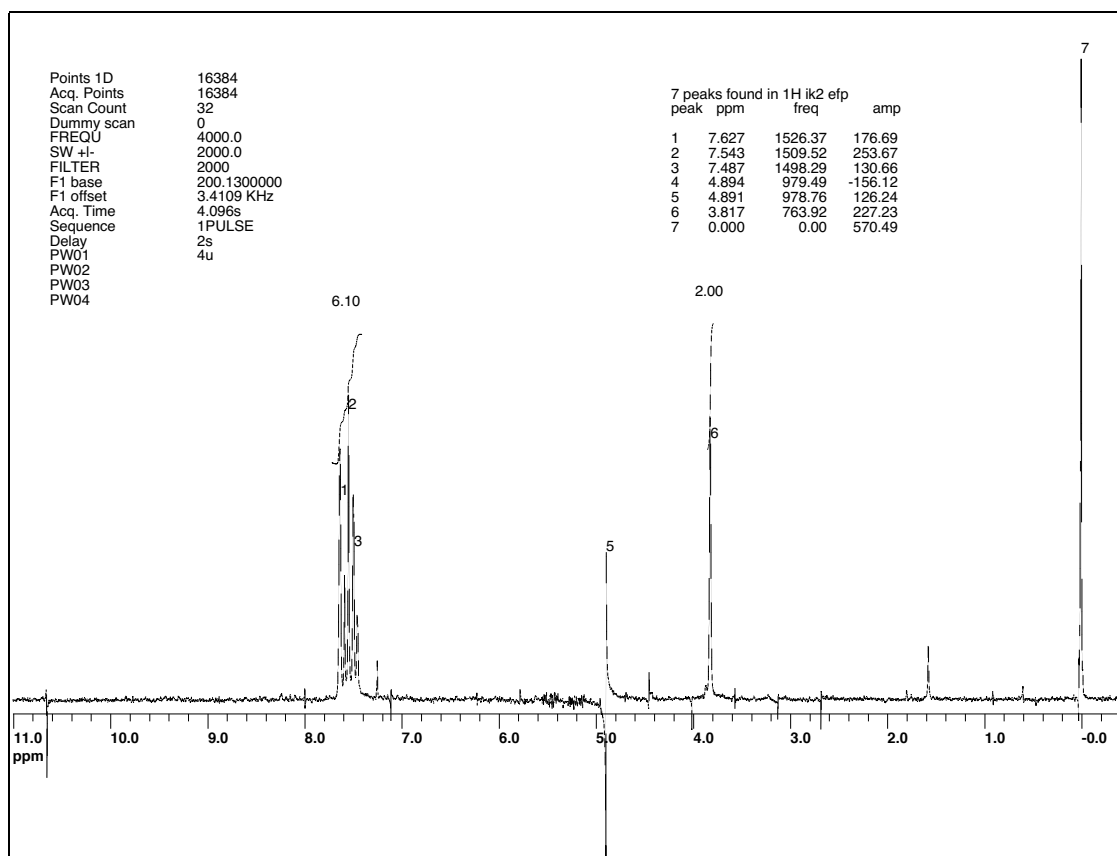


Figure 17.  $^1\text{H}$  NMR spectrum of 2,7-Dibromofluorene **53**.

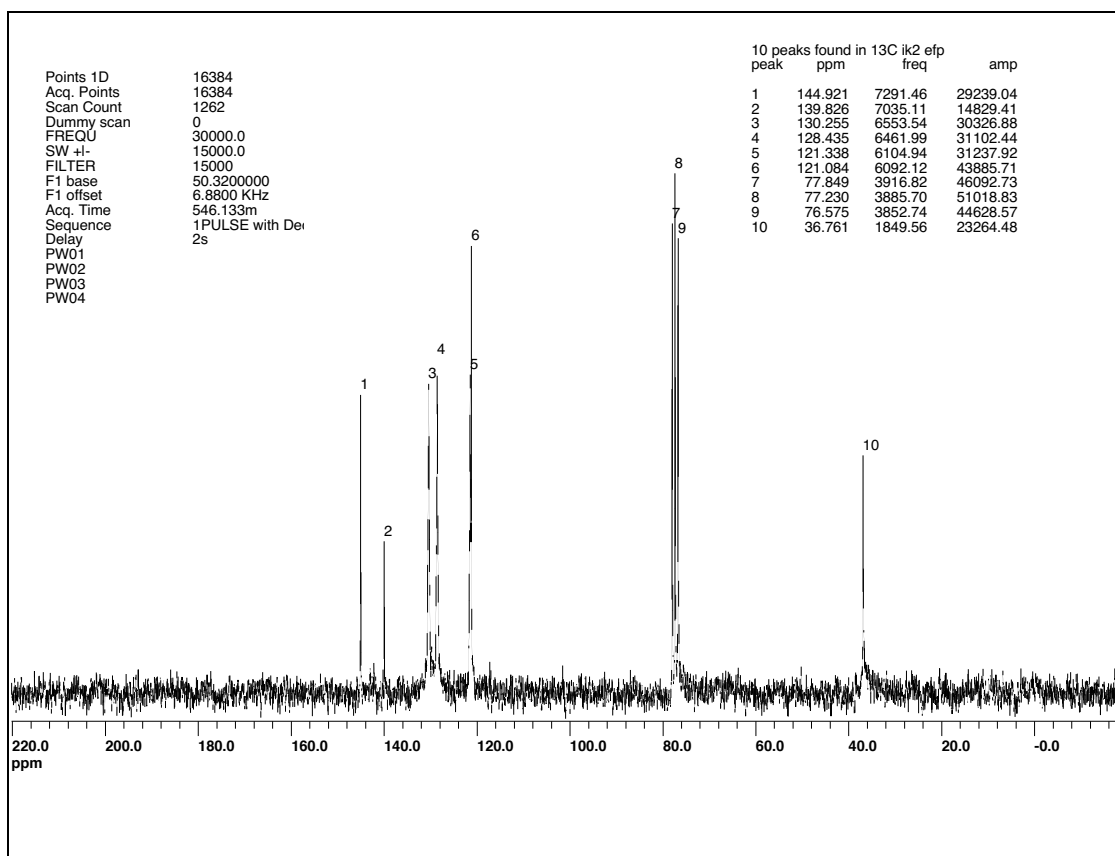


Figure 18.  $^{13}\text{C}$  NMR spectrum of 2,7-Dibromofluorene **53**.

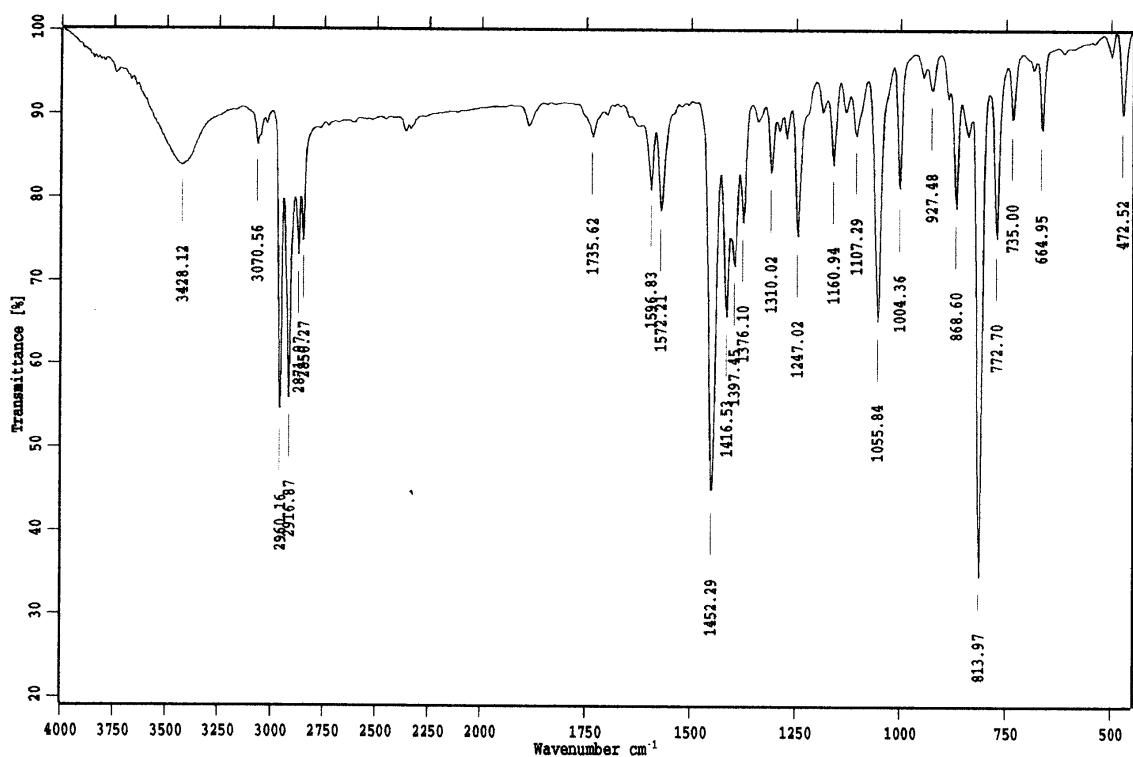
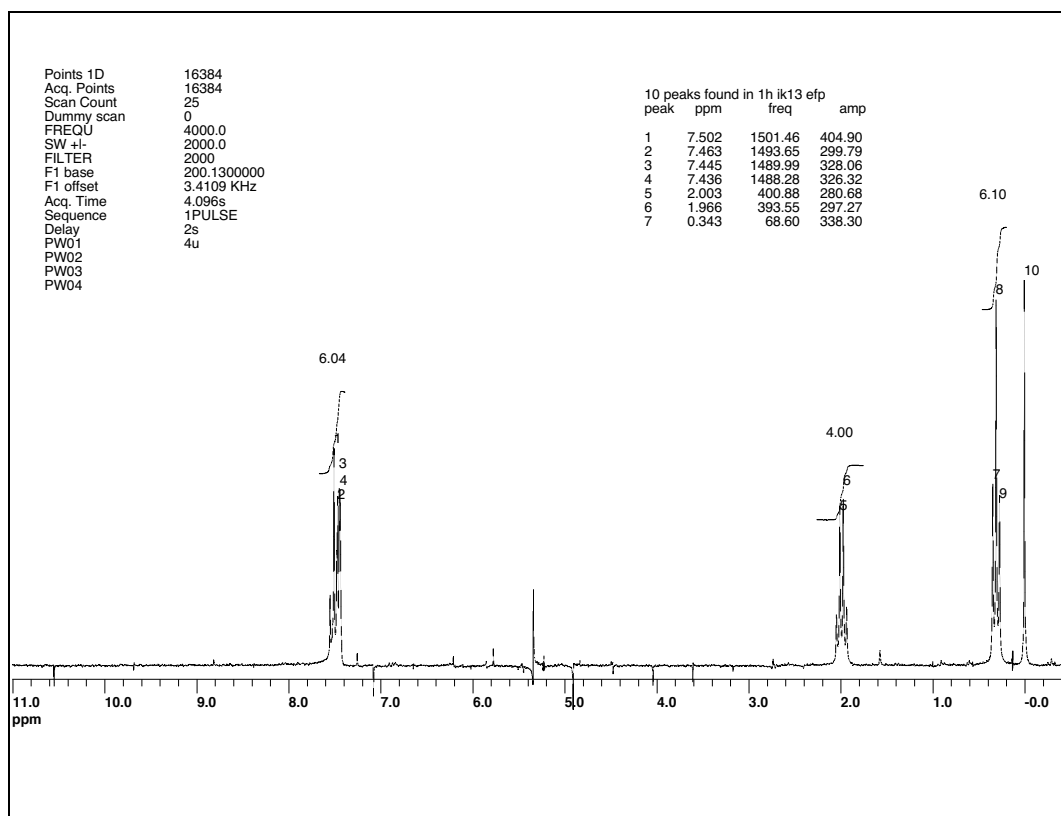
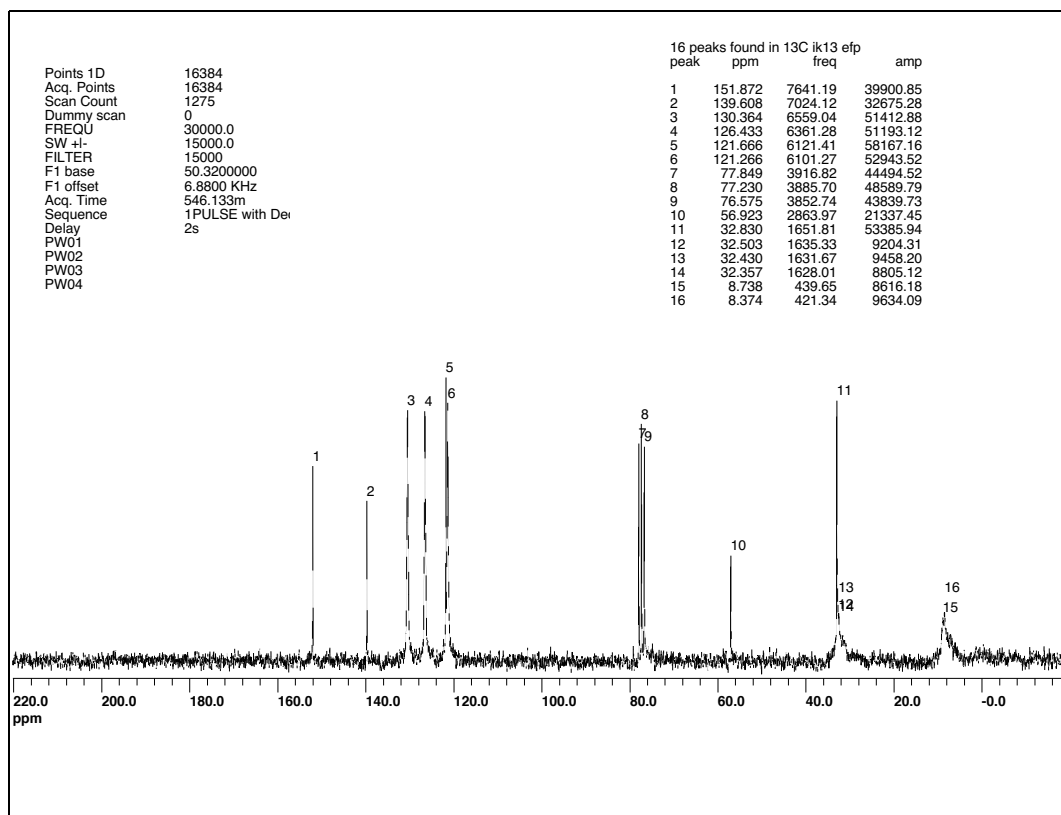


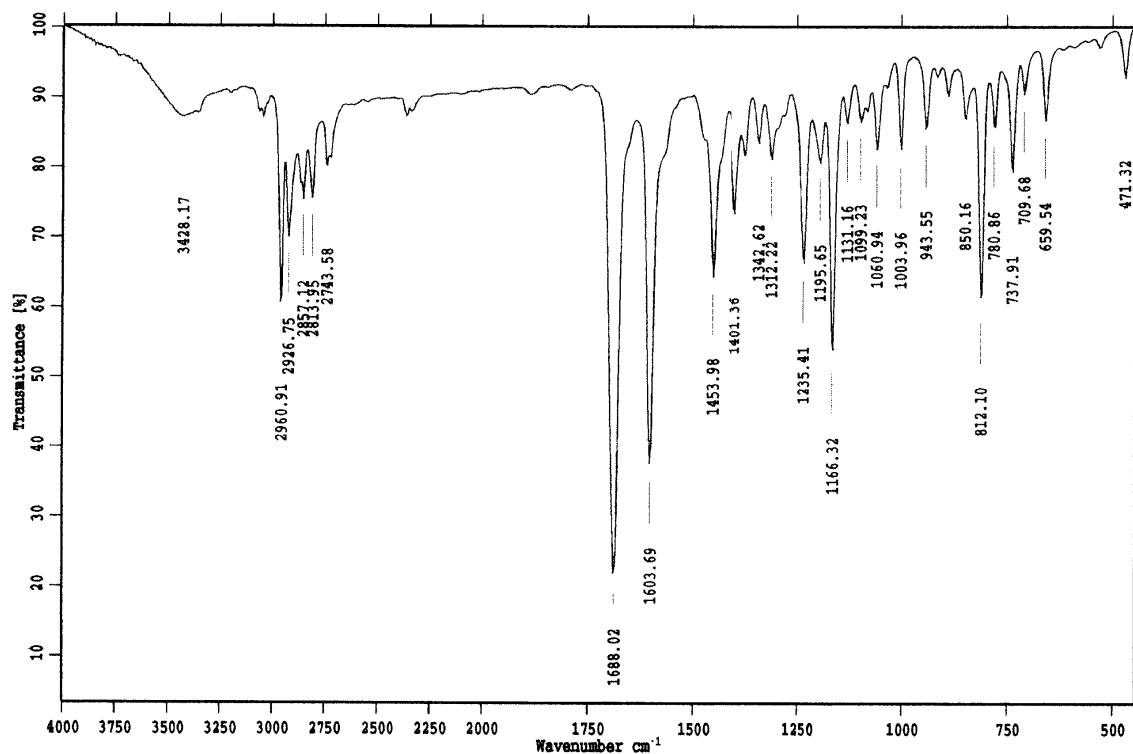
Figure 19. IR spectrum of 9,9-diethyl-2,7-dibromofluorene **3**.



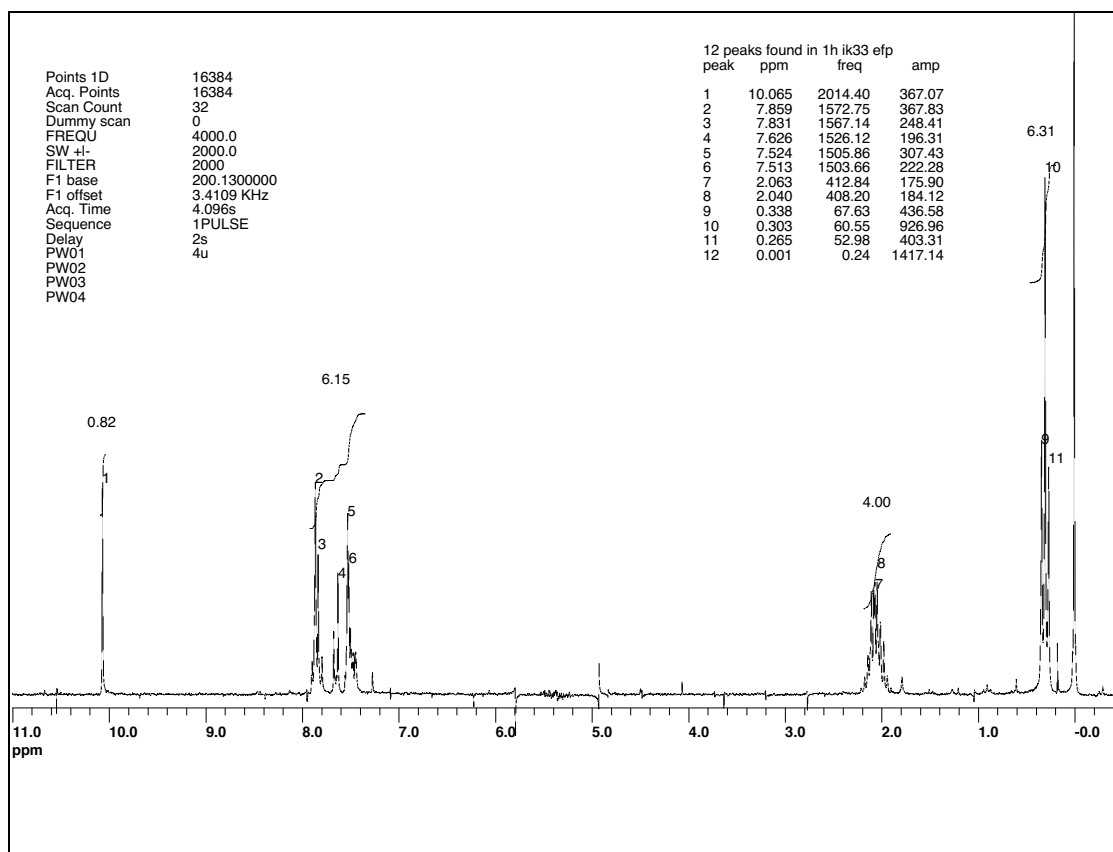
**Figure 20.**  $^1\text{H}$  NMR spectrum of 9,9-diethyl-2,7-dibromofluorene **3**.



**Figure 21.**  $^{13}\text{C}$  NMR spectrum of 9,9-diethyl-2,7-dibromofluorene **3**.



**Figure 22.** IR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene **54**.



**Figure 23.**  $^1\text{H}$  NMR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene **54**.

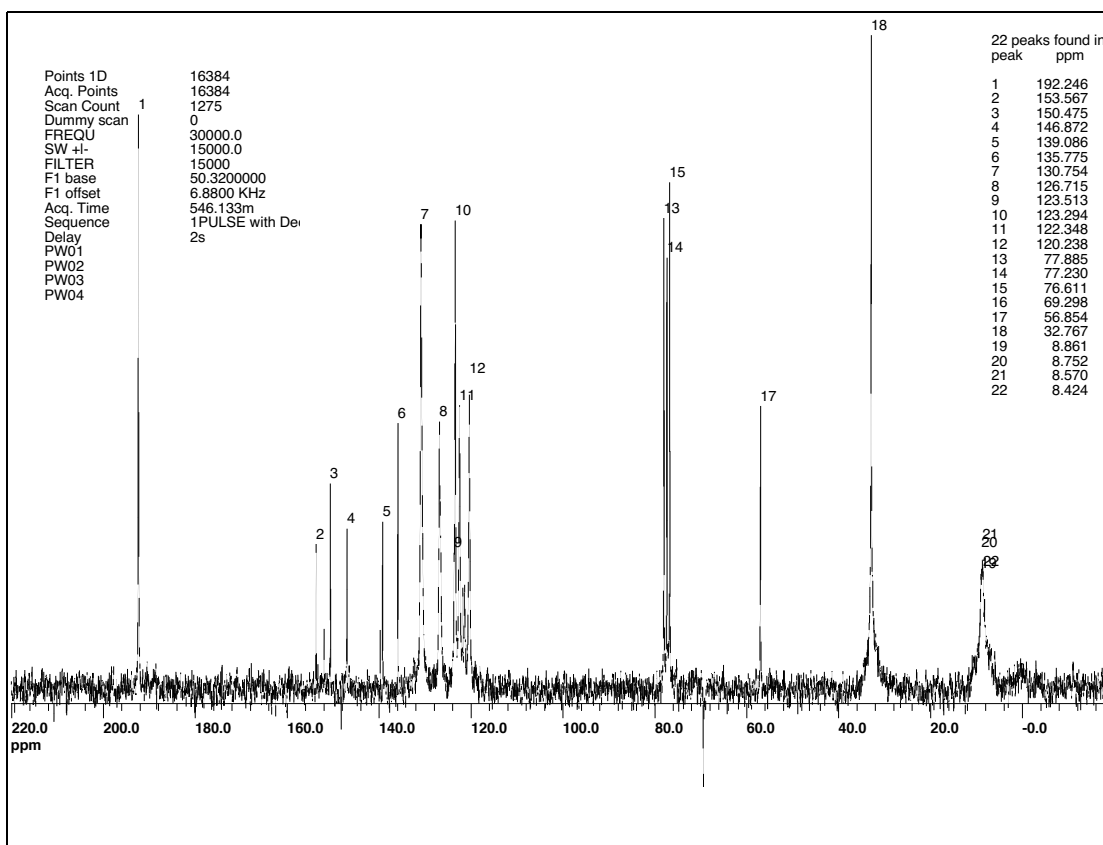


Figure 24.  $^{13}\text{C}$  NMR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene **54**.

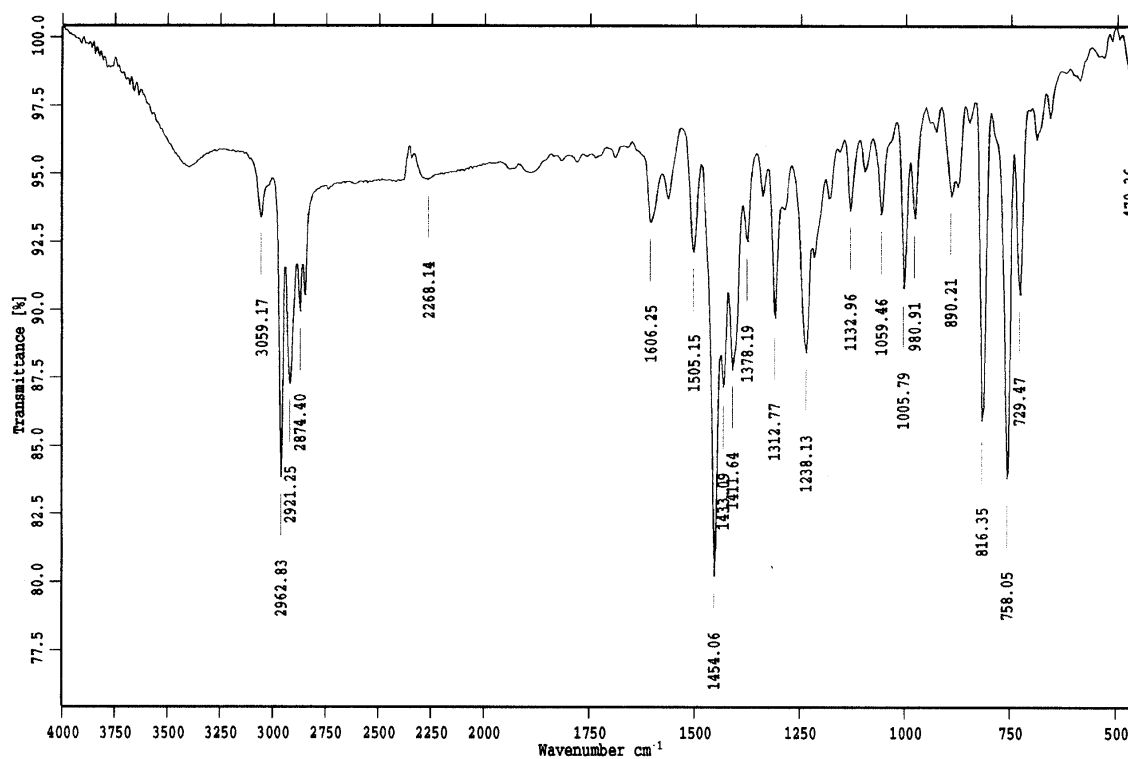


Figure 25. IR spectrum of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55**.

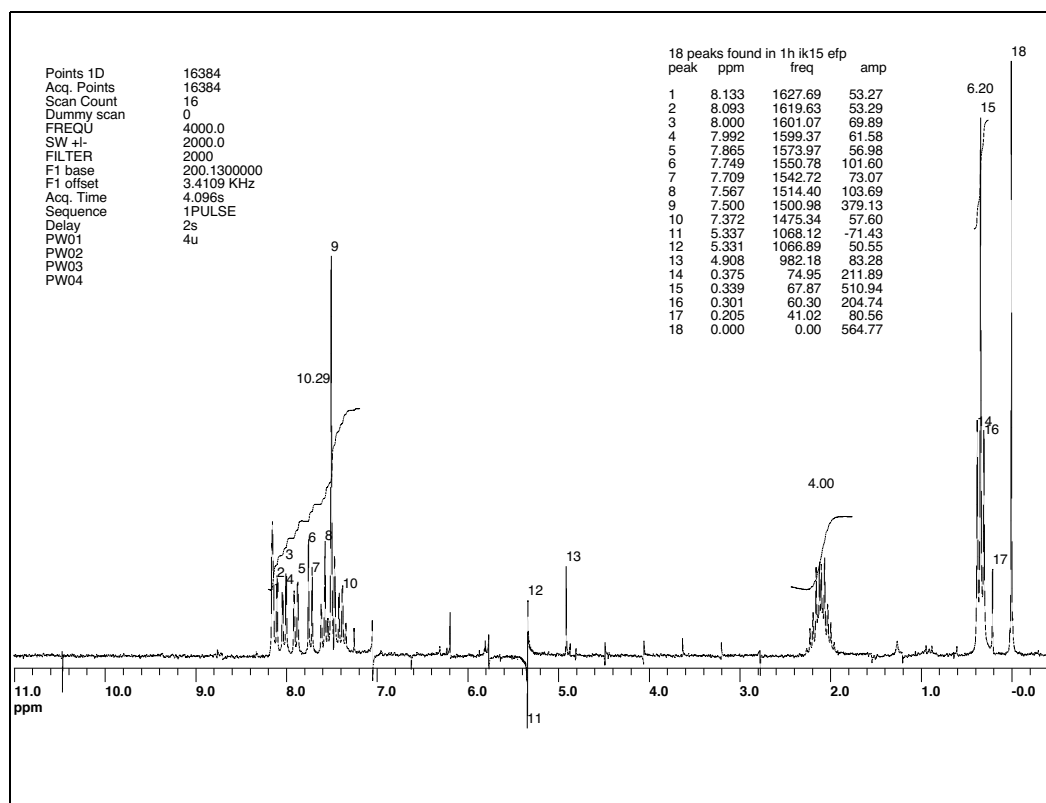


Figure 26.  $^1\text{H}$  NMR spectrum of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55**.

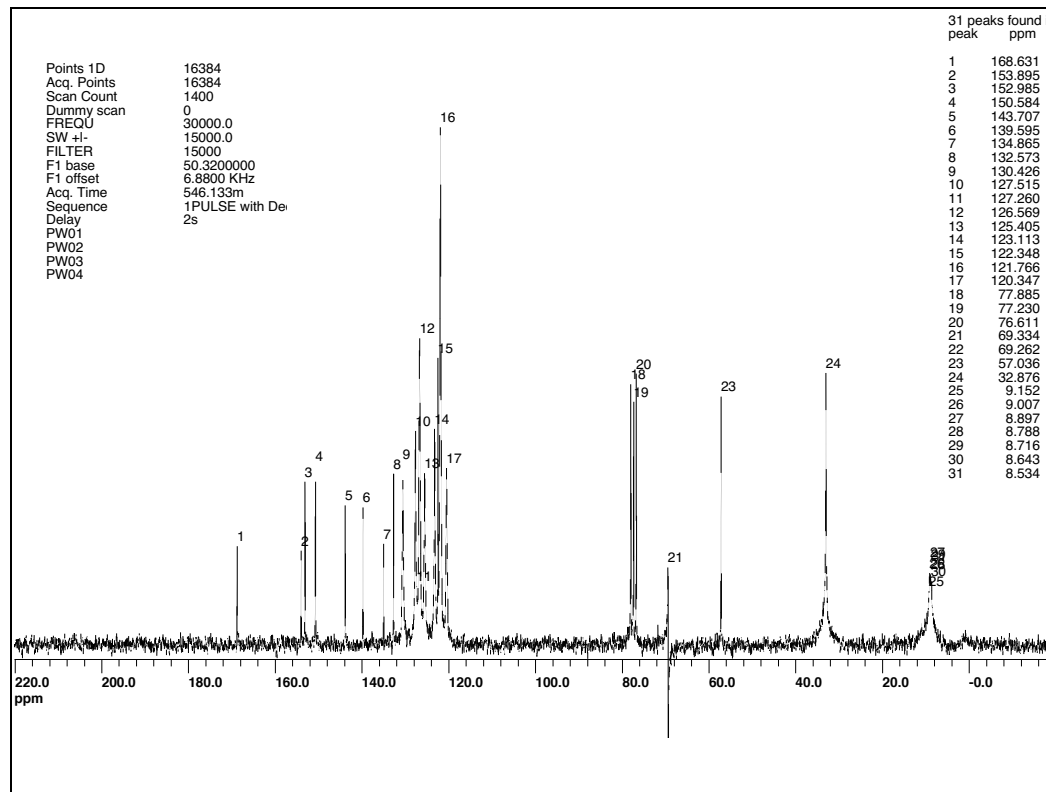


Figure 27.  $^{13}\text{C}$  NMR spectrum of 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole **55**.

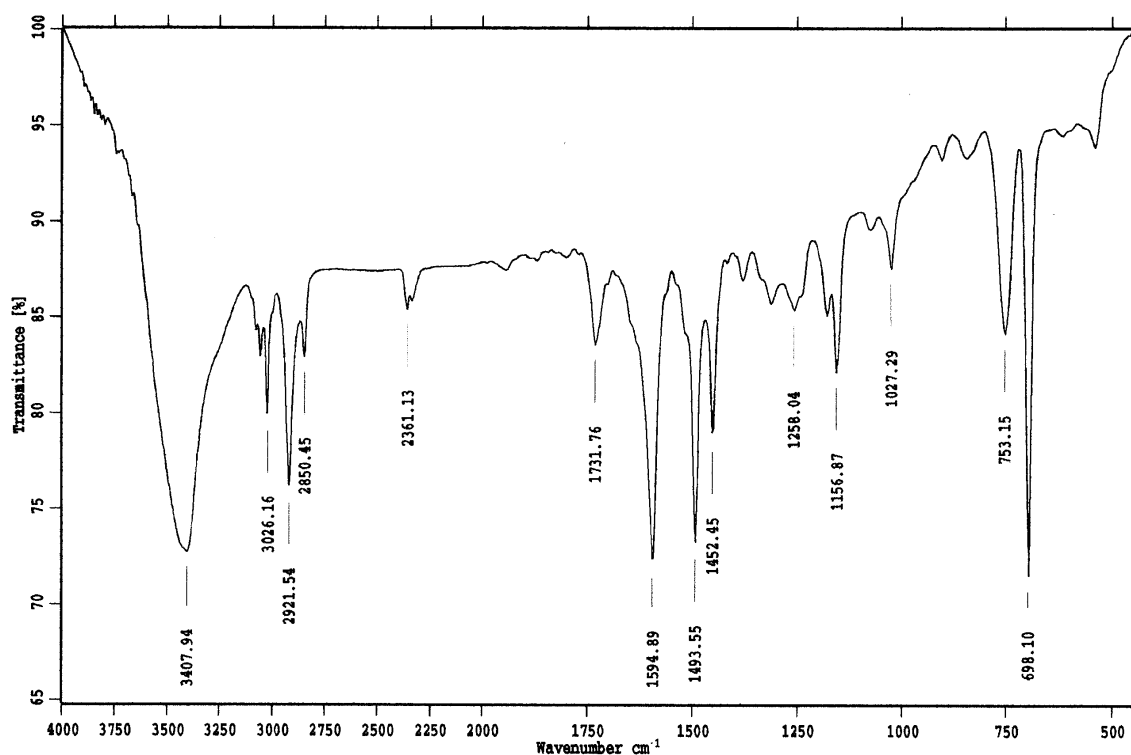


Figure 28. IR spectrum of 3-Benzyloxydiphenylamine **57**.

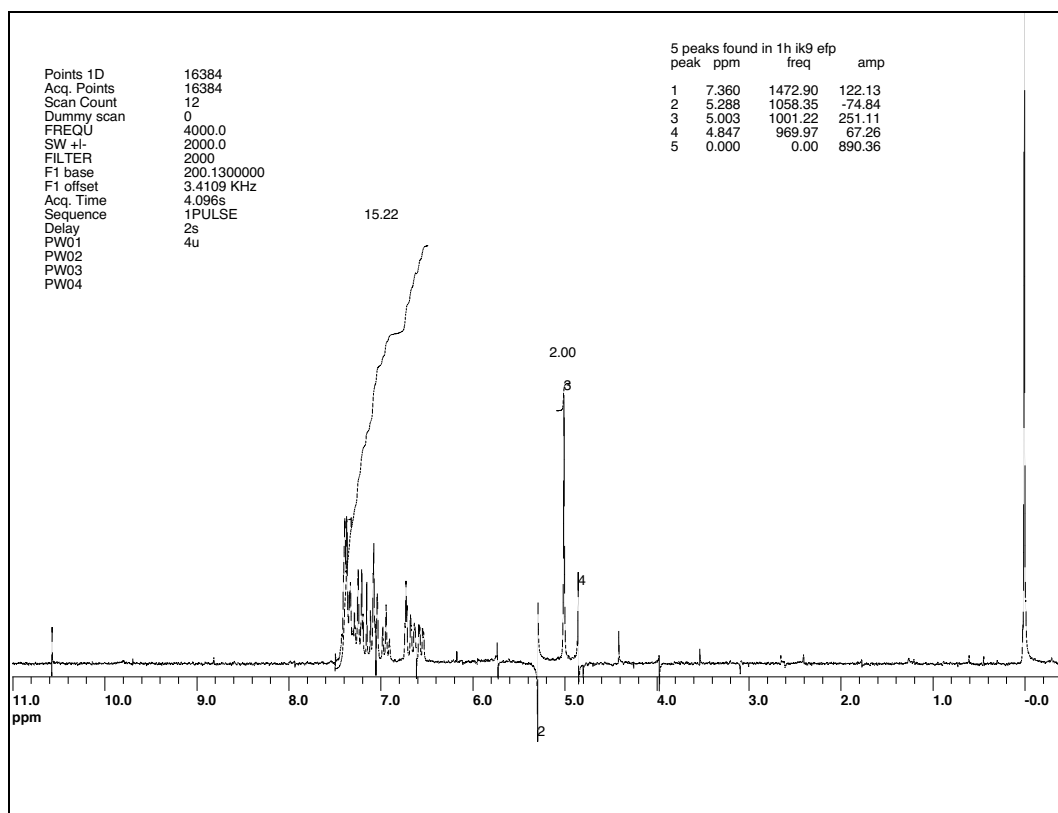
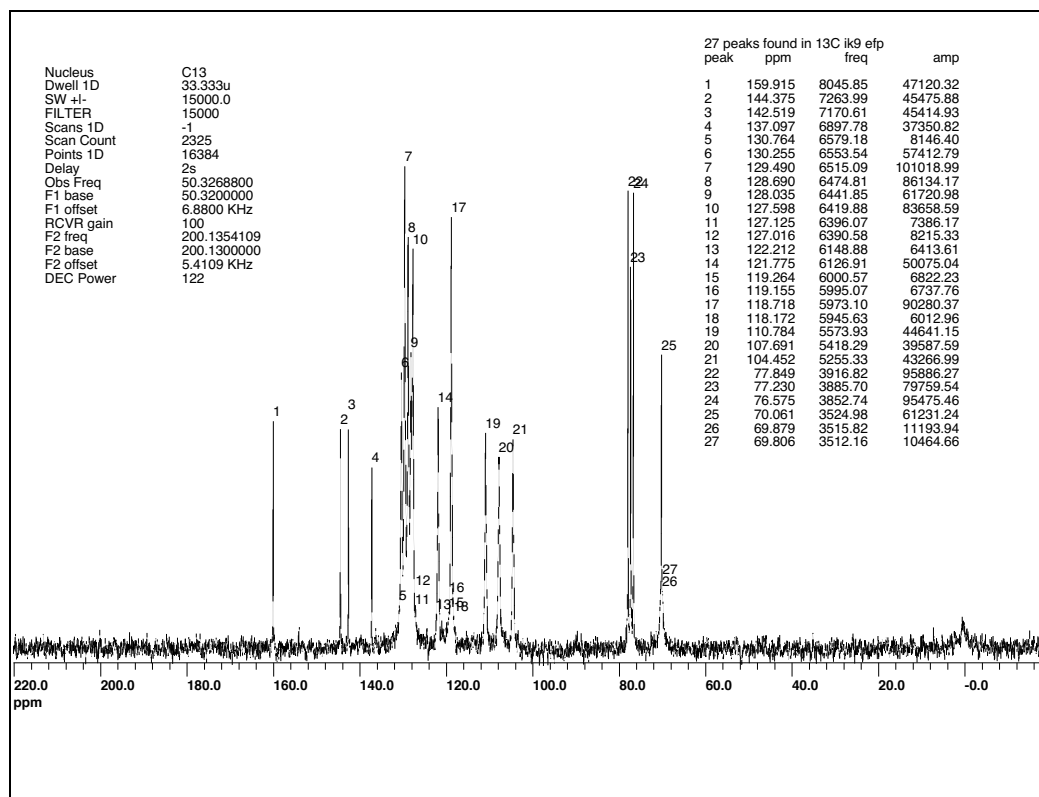
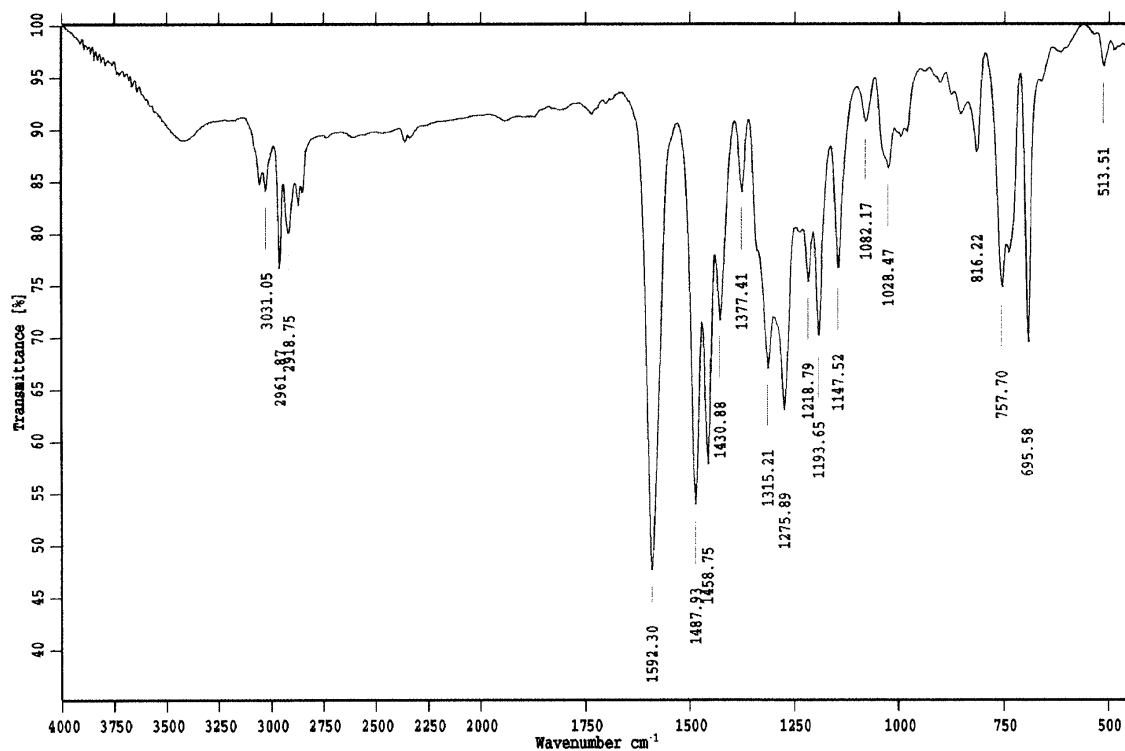


Figure 29.  $^1\text{H}$  NMR Spectrum of 3-Benzyloxydiphenylamine **57**.

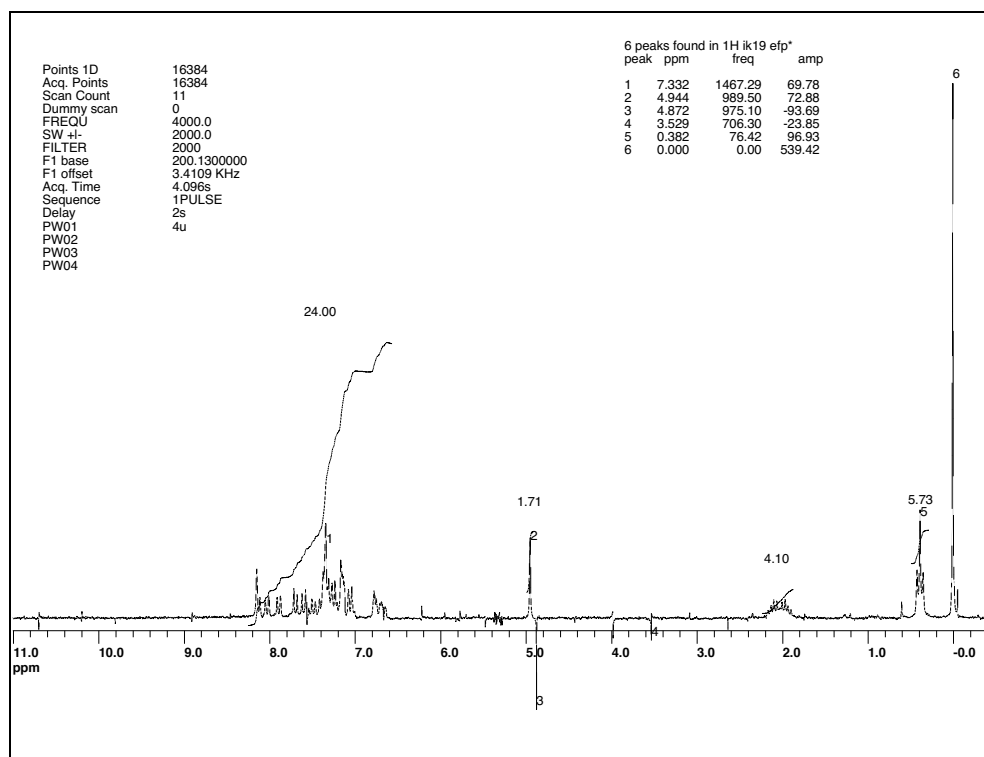




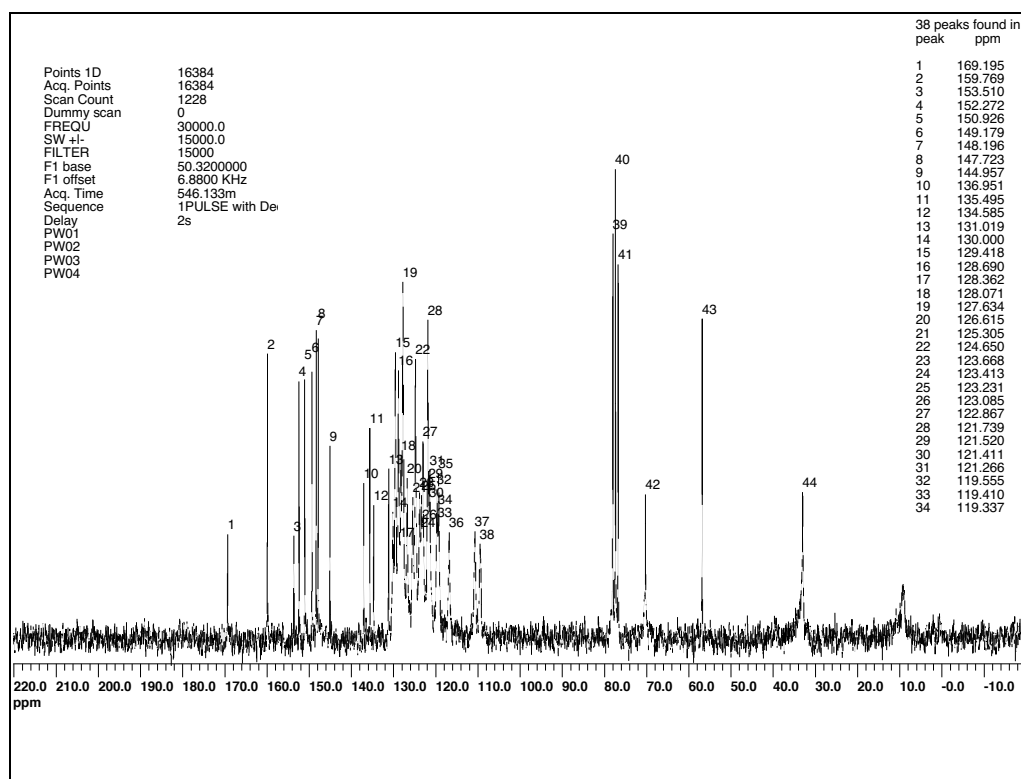
**Figure 30.**  $^{13}\text{C}$  NMR Spectrum of 3-Benzyloxidiphenylamine **57**.



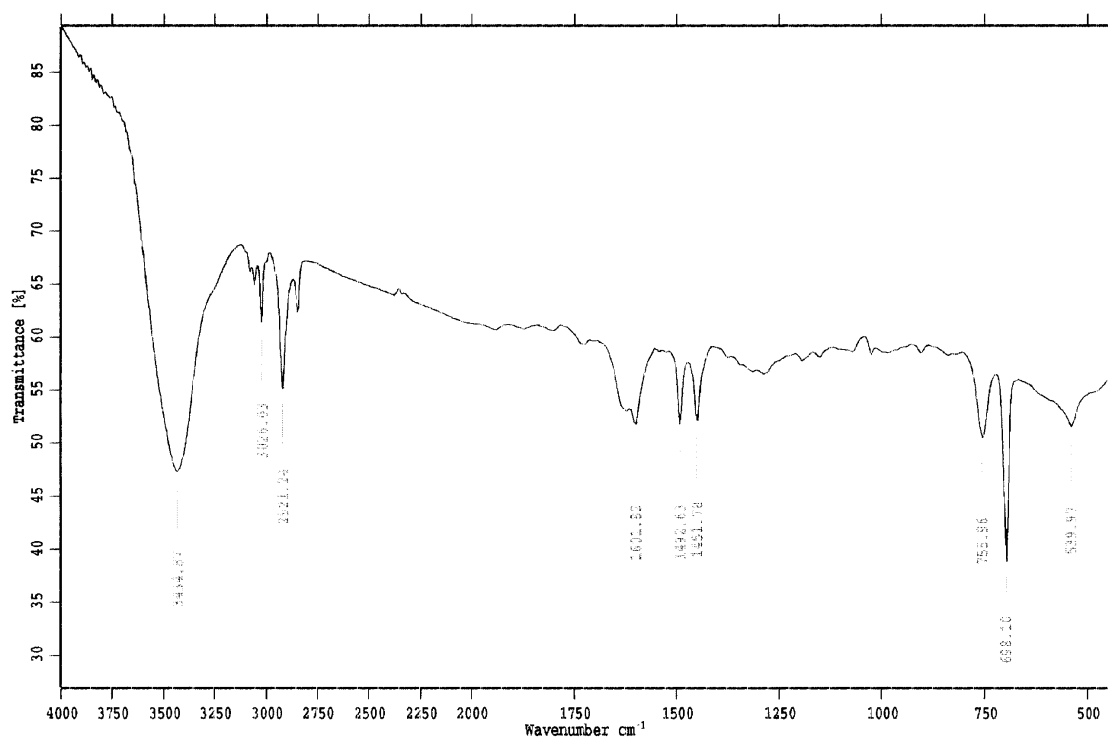
**Figure 31.** IR Spectrum of 2-(7-(3-benzyloxidiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58**.



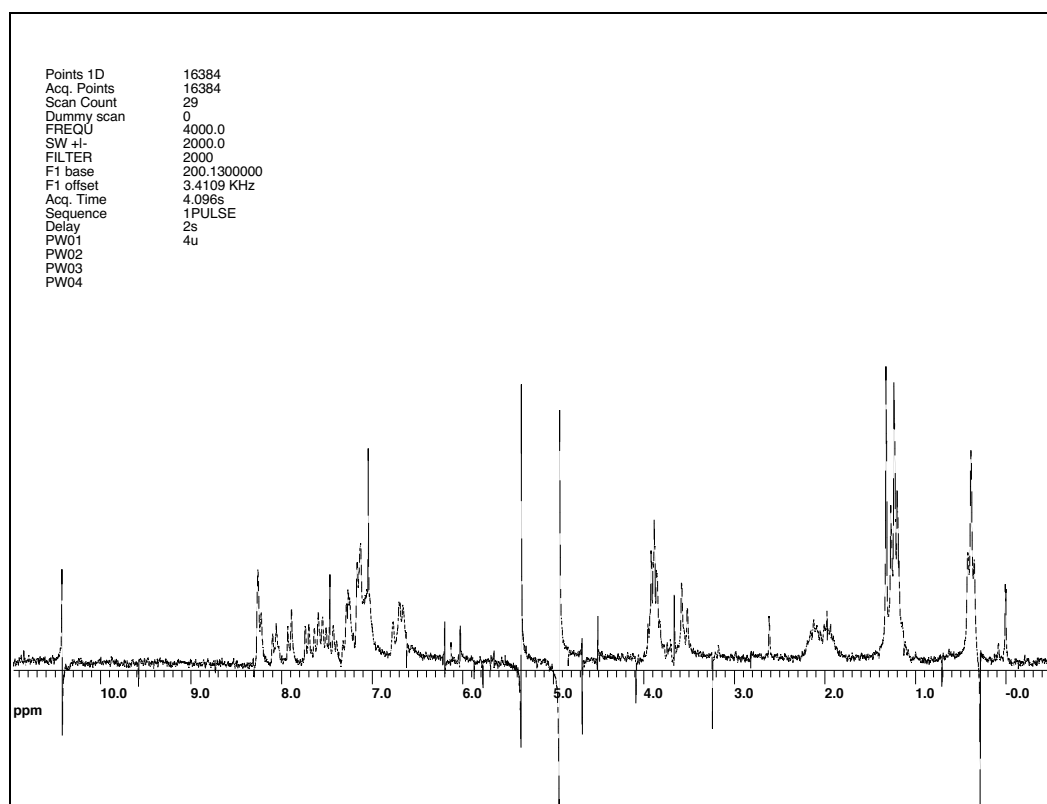
**Figure 32.**  $^1\text{H}$  NMR spectrum of 2-(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58**.



**Figure 33.**  $^{13}\text{C}$  NMR spectrum of 2-(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **58**.



**Figure 34.** IR spectrum of 2-(7-(3-hydroxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **59**.



**Figure 35.**  $^1\text{H}$  NMR spectrum of 2-(7-(3-triethoxysilyloxymethoxy)phenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole **60**.

## **APPENDIX**

The following pages contain images of material presented at the American Chemical Society Dayton Section Poster Session held in Dayton, Ohio in March, 2000.

# *Functionalization of Highly Active Two-Photon Absorbing Chromophores for Advanced Optical Composite Applications*

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## Nonlinear Optical Absorption



Light = electromagnetic field

NLO material responds to em field with a charge separation

- At low power, polarization is linear with respect to field intensity
- At high power, polarization is nonlinear with respect to field intensity

$$P = \chi^{(1)} E + \chi^{(2)} E E + \chi^{(3)} E E E + \dots$$

Composed of both nonresonant and resonant terms

$\chi^{(3)}$

Resonant effects -

- One photon - results in a change in RI due to heating
- Two photon -

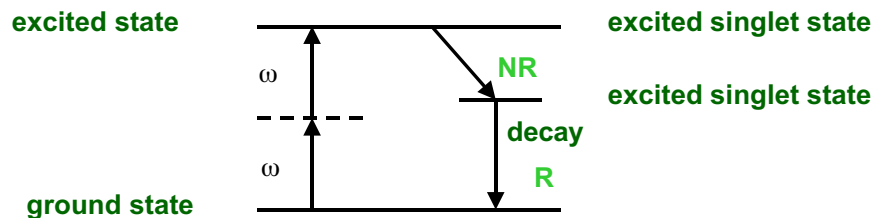


## Two Photon Absorption



### Basic Concepts:

- material with an electronic excited level  $2\omega$  of input laser
- simultaneous absorption of two photons
- light with higher frequency is released i.e. conversion



## Applications



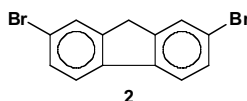
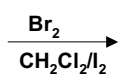
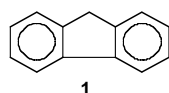
Dyes with increased cross sections and fluorescence led to:

- two photon upconverted lasing, two photon optical limiting, 3D optical data storage, and photodynamic therapy
- Focus: 3D imaging two-photon laser scanning confocal microscopy
  - peak must occur at or around 800 nm
  - useful material for optical power limiting
  - Nondestructive evaluation (NDE) of aircraft paint

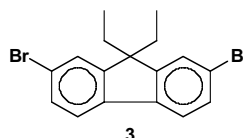
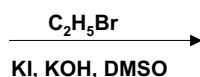




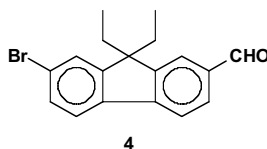
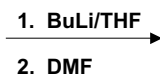
## Synthesis of 2-Bromo-7-formyl-9,9-diethylfluorene



Yield = 99%  
mp = 156-159.3°C  
m/z = 324 (M<sup>+</sup>)



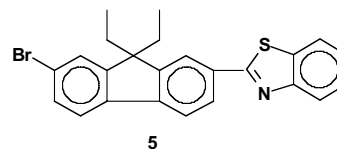
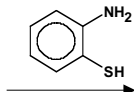
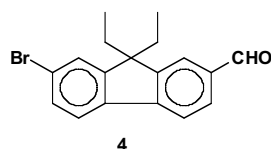
Yield = 69%  
mp = 153-155°C  
m/z = 380 (M<sup>+</sup>)



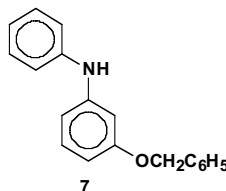
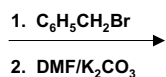
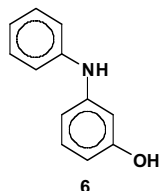
Yield = 82%  
mp = 128.3-130°C  
m/z = 329 (M<sup>+</sup>)  
IR: C=O stretch 1688 cm<sup>-1</sup>



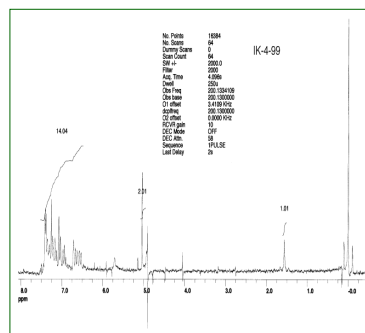
## Starting Materials



Yield = 82.1%  
mp = 131-133°C  
m/z = 434 (M<sup>+</sup>)

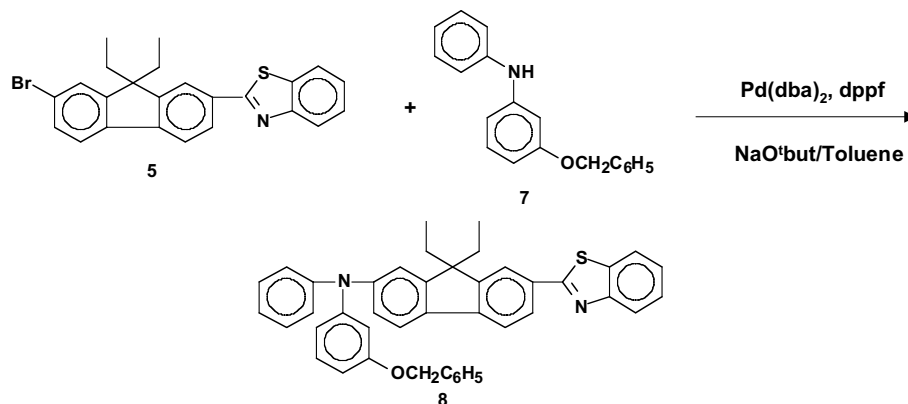


Yield = 88% mp = 53-55°C m/z = 275 (M<sup>+</sup>), 198 (M-C<sub>6</sub>H<sub>5</sub>)  
Calcd for C<sub>18</sub>H<sub>17</sub>NO : C; 82.86, H; 6.23, N; 5.09  
Found C; 82.76, H; 6.22, N; 5.02





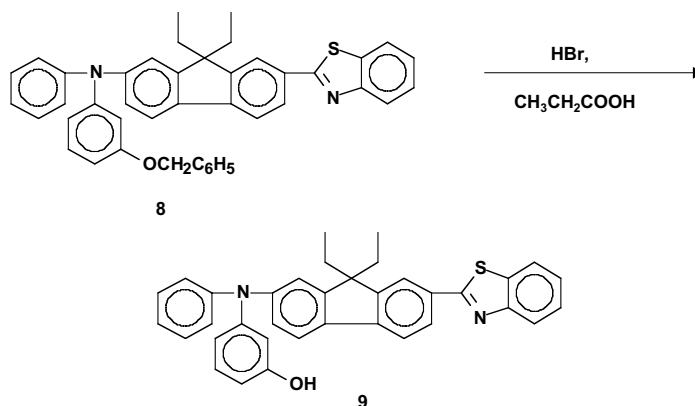
## Amine Coupling



Yield = 75% mp = 178-180°C  
m/z = 628 (M<sup>+</sup>) Calcd for C<sub>43</sub>H<sub>36</sub>N<sub>2</sub>OS C; 82.12, H; 5.77, N; 4.46, S; 5.10  
Found C; 82.23, H; 5.84, N; 4.33, S; 5.08



## Deprotection



Yield = 75%  
mp = 244-245°C; IR = 3440 cm<sup>-1</sup> OH stretch





## Summary



- The addition of the benzyl protective group to 3-hydroxydiphenylamine provided 3-phenoxydiphenylamine
- 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole was synthesized.
- 2-(7-(3-phenoxydiphenylamino-9,9-diethyl-2-fluorenyl)benzothiazole was synthesized.
- The benzyl protective group was successfully removed from 2-(7-(3-phenoxy)-diphenylamino-9,9-diethyl)-2-fluorenyl)benzothiazole.
- 3-phenoxydiphenylamine and 2-(7-bromo-9,9-diethyl-2-fluorenyl)benzothiazole.
- Future Work: Addition of 2-(7-(3-phenoxy)-diphenylamino-9,9-diethyl)-fluorenyl benzothiazole into a silicon matrix.

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## **VITA**

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